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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

D. Mendeleeff

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SOME PROBLEMS OF CONTEMPORARY INORGANIC CHEMISTRY IN THE LIGHT OF THE IDEAS OF D. I. MENDELEEV

S. M. Ariya

(On the 50th Anniversary of the Death of D. I. Mendeleev)

February 2 marked the 50th anniversary of the death of the great Russian chemist D. I. Mendeleev. Far ahead of his time, D. I. Mendeleev put forward a number of extremely important ideas and made discoveries which have had an enormous influence on the subsequent development of chemistry, physics and a number of related fields.

Undoubtedly the greatest discovery of D. I. Mendeleev, and the one which has made his name immortal, is the discovery of the periodic law.

Many great scientists have devoted their studies to the history of the discovery of the periodic law, to an analysis of the process by which the genius, its author, conceived his ideas, to the question of the subsequent development of these ideas in contemporary science, and to an evaluation of the significance of the periodic law and of other theoretical viewpoints put forward by D. I. Mendeleev. The high regard with which that great thinker, F. Engels, viewed the discoverer of the periodic law, is well known.

In the present short article we propose to examine only a few of the problems related to the development and contemporary state of the periodic law.

The periodic law is a law of a special type. It is in fact a whole complex system of ideas concerning the relationship between the properties of the elements and the place which they occupy in the natural system of the elements drawn up by D. I. Mendeleev. The periodic law, inexhaustible in its depth, cannot be expressed by any sort of single mathematical formula. This probably partly explains the fact that certain errors in its understanding have persisted to the present day. A number of these errors are well known. We shall also pause over some of these.

At one time, for example, the idea was put forward that the periodic law was a natural consequence of Pauli's principle. The obvious nature of this mistake has been pointed out by a number of authors. It is of course true that the Pauli principle and the regularities of the change in the quantum numbers of the electrons in atoms, have a direct relationship to the periodic law. But neither Pauli's principle, nor the other regular relationships governed by the structure of the electron clouds, cover, of course, all the simple laws of nature on which the periodic system is based. The latter is also related to the laws which govern the structure of the atomic nucleus and to the laws of the chemical bond and the principles of thermodynamics and statistics.

The periodic law goes much deeper than the Pauli principle and embraces a much wider range of phenomena than the latter.

At the present time it is generally accepted that all the properties of both elementary and compound substances undergo a regular change throughout the periodic system. At the same time it is well known that as the complexity of a chemical substance increases, these regularities likewise become more and more complex. This was very clearly expressed by D. I. Mendeleev himself: "The periodic law gives the properties of the elements, and not those of the elementary states of matter."* There are a number of other well-known pronouncements made by D. I. Mendeleev, in which he says that the periodicity in the properties of elementary and compound substances is shown precisely because of the fact that these properties are determined by the properties of the elements from which they are formed.

*D. I. Mendeleev. Principles of Chemistry. Edition V (1889), Note 11, Chapter XV

These ideas of D. I. Mendeleev have been brilliantly confirmed during the subsequent development of chemistry. Indeed, at the present time it is well known that the change in the properties of the isolated particles – atoms and ions – illustrates the periodic law in its clearest, "purest" form.

To this is related such properties as the very important characteristics of atomic spectra, the magnetic moments of atoms and ions, and, as S. A. Shchukarev has emphasized, their energy characteristics. An analysis of the fundamental energy characteristics of atoms and ions, the energies of the step-wise removal of electrons from the atoms of all the elements of the periodic system, carried out by S. A. Shchukarev, gave him grounds for declaring that this picture of the periodicity in the properties of the electron clouds in the system of the elements "... is now to be preferred to a comparison of the forms of chemical compounds as the primary characteristic of the periodic law."**

Indeed, if we turn to Figure 1, which is taken from the article by S. A. Shchukarev just cited, the quotation becomes quite clear. This Figure shows the relationship between the magnitude of the first ionization potential and atomic number. It is important at the same time to note that if we take not the magnitude of the first ionization potential but the magnitudes of the second, third, fourth ..... nth ionization potential, then, as is perfectly natural, the same clear periodicity is observed. As an example, Figure 2 shows the change in the eighth ionization potential of the elements, with atomic number. At the same time the view is often expressed that periodicity is associated with the periphery of the atom and does not concern the inner electrons closest to the nucleus, whose properties change linearly with increase in atomic number.

This error was revealed some years ago by S. A. Shchukarev, who showed the reasons for its appearance.

Arguments in support of the idea that there is no periodicity in the properties of the inner electrons are usually based on the linear relationship between the square root of the vibration frequencies corresponding, for example, to the $k\alpha$ lines in the x-ray spectra and the atomic number, which was established, as is well known, by Moseley. The linear character of this relationship, i.e., the absence of periodicity, is however due to the fact that in this case we are concerned with changes in the energies of an electron for a single set of values of the quantum numbers as the atomic number is increased. With this condition imposed, the energy of the bond linking the electron to the nucleus will of course vary linearly with the magnitude of the charge on the nucleus.

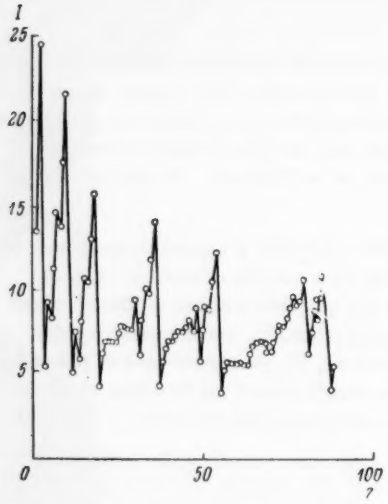

Fig. 1. Relationship between the magnitude of the first ionization potential (in electron-volts) and atomic number (z).

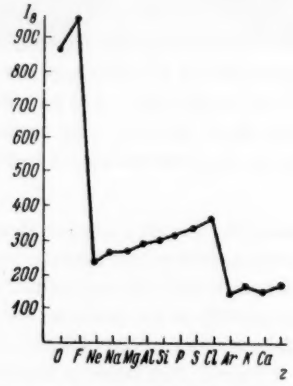

Fig. 2. Relationship between the magnitude of the eighth ionization potential (in electron-volts) and atomic number (z).

If however, we consider, for example, ionization potentials of any desired high order (tenth, twentieth, thirtieth. . . .), they prove to be a periodic function of the atomic number, since in this case we are dealing with electrons with a different set of quantum number values. Thus the regular variation established by Moseley in no way indicates the absence of periodicity in the inner electron clouds, but the latter is related to the separation of the electron clouds into sub-levels and to the

** S. A. Shchukarev, Bull. Leningrad State University, No. 11, 127 (1954).

change in the quantum numbers of the electrons as they are added to the atom around the nucleus. The periodicity is thus associated with the whole electron cloud of the atom: with both its periphery and its inner levels. In particular, the values of the ionization potentials for the atoms of O, F, Na, Mg, Al. . . , given in Figure 2, are related to inner electron clouds and the periodicity in their change is quite clearly shown.

The clear manifestation of the periodic law in the energy relationships of the isolated atoms and ions is important not only in itself, but also because the regularity of the change in the ionization potentials in the periodic system is directly reflected in the properties of binary compounds, and of ions in solution, etc.

Below we give a short review of some of these points.

The Phenomenon of Secondary Periodicity

Figure 3 shows the change in the sum of the first five ionization potentials for the atoms of the elements of the main sub-group of Group V. It is clearly seen that this quantity shows not a linear but a periodic variation from nitrogen to bismuth. This is shown by a sharp fall from nitrogen to phosphorus, followed by a gradual descent to arsenic, after which there comes another steeper descent to antimony and finally an ascent to bismuth.

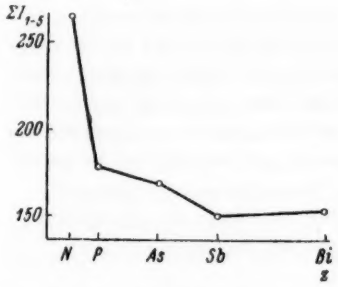

Fig. 3. The change in the sum of the first five ionization potentials (in electron-volts) of the atoms of the elements in the main sub-group of Group V.

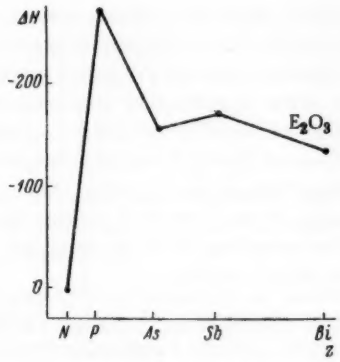

Fig. 4. The change in the heats of formation of the oxides of type E_2O_3 (in kcal. /mole) formed by the elements of the main sub-group of Group V.

This feature is directly related to the important phenomenon of secondary periodicity in the properties of the elements in the main sub-groups, discovered in 1915 by E. V. Biron.

A lack of knowledge of the important work of E. V. Biron has led a number of authors to a somewhat primitive understanding of the periodic law. It is often stated that the properties of the elements in the main sub-groups change linearly with atomic number. In fact this is not the case. As an example we need only look at the heats of formation of the oxides of the type E_2O_3 formed by the elements of the main sub-group of Group V (Figure 4). It is quite apparent that this important property of these compounds, their heat of formation, does not show a linear change as we descend the sub-group.

The phenomenon of secondary periodicity has in recent years attracted the attention of a number of authors: Hillebrand, S. A. Shchukarev, A. F. Kapustinsky, Kh. Balarev, V. P. Shishokin, Lakotos etc.

S. A. Shchukarev and Hillebrand were the first to point out that the phenomenon of secondary periodicity in the heats of formation of the binary compounds of the elements of the main sub-groups is a direct reflection of the periodic change in the values of the ionization energies of the atoms of the elements in the main sub-groups on moving within them from top to bottom.

S. A. Shchukarev has pointed out at the same time that D. I. Mendeleev himself took account of the non-linear change in the properties of the elements of the main sub-groups as they are descended from top to bottom; it was not by chance that, when estimating the properties of the elements whose existence he predicted, he interpolated them not only vertically, but also horizontally, in order to reduce the inaccuracy due partly to

this very phenomenon of secondary periodicity.

The secondary periodicity in the heats of formation of the binary compounds formed by the elements in the main sub-groups is superimposed on the main periodicity observed in the change in the energy characteristics of both elementary and compound substances. It is well known that even when the periodic system was being established, at a time when thermochemical data were as yet very scarce, D. I. Mendeleev pointed out the connection between these data and the place of the element in the periodic system.

A. F. Kapustinsky has noted that the thermochemical logarithmic rule, which he has enunciated and according to which the heat of formation of the compounds of elements whose atoms have similar electronic configurations is a linear function of the logarithm of the atomic number, is often complicated by the existence and extensive manifestations of the phenomenon of secondary periodicity.

The phenomenon of secondary periodicity in the properties of the compounds of elements in the main sub-groups of the periodic system results from the structure of the periodic system itself. The periodic change in the energy characteristics of the isolated atoms and ions of the elements of the main sub-groups, which forms the foundation of the system, is linked, as S. A. Shchukarev has shown, with the filling, in the appropriate places in the periodic system, of the d- and f-levels of the electron clouds, which brings about a strengthening of the attraction between the nucleus and the outer s- and p-electrons.

Without going into a detailed examination of the phenomenon of secondary periodicity in the heats of formation of binary compounds of the elements in the main sub-groups, we will at this stage point out only the fact that the relation between it and the secondary periodicity in the magnitudes of the ionization energies of the atoms is not always of the same character. In those cases when the compound even only partly approaches the ionic state, so that the elements of the appropriate main sub-group approach the cationic condition, the reasons for the phenomenon of secondary periodicity are clear. In this case the ionization energy of the atoms is one of the terms in the algebraic sum by which the magnitude of the heat of formation may be expressed. Since the ionization energy of the atoms is a periodic function of atomic number, then when the appropriate changes take place in the remaining terms the total sum, i. e., the heat of formation, will show a periodic change with increase in atomic number.

The reasons for the phenomenon of secondary periodicity in the case where the compounds are clearly not ionic are more complex. To take a particular example, the change in the magnitudes of the heats of dimerization of the diatomic molecules of the elements in the main sub-group of Group V: $2E_2 \rightarrow E_4$, is of a periodic character. The change in the values for these elements is given in Figure 5.

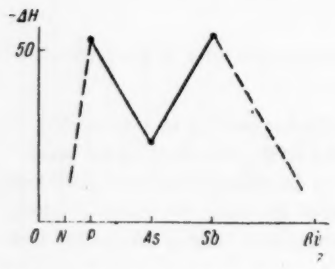

Fig. 5. The change in the heats of dimerization of the diatomic molecules of the elements in the main sub-group of Group V (in kcal.).

The E_4 molecules are most stable in the case of phosphorus and antimony, i. e., in those elements in which the pentavalent state is the most stable. Molecules of the type E_4 have never been detected for nitrogen and bismuth. If they do exist, they are extremely unstable, which indicates an extremely low value for the heats of dimerization of the N_2 and Bi_2 molecules. This gives us grounds for directing the appropriate parts of the curve in Figure 5 downwards (the absence of experimental data requires us to indicate these parts by dotted lines).

This fact enables us to suggest that the reason for the periodic change in these values is the excitation of higher valence states in their formation, and the energies of excitation should have values which change periodically as the atomic number increases (since the graph of their change should be of the same shape as that of the change in ionization energies), which may give rise to the periodic change in the heats of formation of the appropriate compounds. Thus the direct mechanism of the reflection of the properties of the isolated atoms in the properties of even the comparatively simple binary compounds may be of a very varied character depending on the nature of the chemical bond in the compounds and on their chemical structure.

The change in the heats of formation of the hydrogen compounds, as foreseen by E. V. Biron, is evidently not governed by the law of secondary periodicity, or else it is shown very indistinctly in this case. The change in the values of the enthalpies of formation of compounds, formed by the elements in the main sub-groups with metals, is of a complex nature. Thus, for example, together with a very clear manifestation of the rule of secondary periodicity in the change in the heats of formation of the compounds of zinc with the elements of the main sub-group of Group V, there is an almost complete absence of secondary periodicity in the case of the compounds formed by magnesium with the same elements.

Thus it seems to us proper to emphasize the complexity of the nature of the change in properties of the elements in the main sub-groups as they are descended from top to bottom, a complexity which, if ignored, sometimes leads to a certain primitiveness of approach to the periodic law.

As we have already pointed out above, the secondary periodicity of the heats of formation of binary compounds is one of a very large number of regularities in the change in the magnitudes of the thermodynamic functions of elementary and compound substances.

In particular, the fact that the entropy of elementary and compound substances is a periodic function of atomic number has been pointed out by A. F. Kapustinsky.

The Composition of Binary Compounds

The enormous importance attached by D. I. Mendeleev to the composition of chemical compounds, which, in the period when the periodic law was being established, he considered, along with the atomic weight, as one of the fundamental properties of the elements, is well known. "The chief interest of chemistry lies in the study of the fundamental properties of the elements, and since their nature is as yet quite unknown to us and since we as yet know only two . . . .measureable properties for them: the ability to give compounds of known composition and that other property which we call the weight of the atom . . ." *

At the present time science knows many other quantitative characteristics of the elements which can be precisely determined, but the question of the composition of the compounds formed by the chemical elements remains, of course, one of the foremost questions in chemistry.

D. I. Mendeleev, by formulating the important principles of saturation, and substitution, and the even-number rule, laid the foundations for the subsequent, as yet unfinished, study of the composition of chemical compounds.

We give below a very short review of some of the regularities governing the composition of binary compounds.

As the factual material of inorganic chemistry increases, there is an increase in the number of compounds whose composition does not correspond in detail to those compositions which D. I. Mendeleev considered as characteristic of the different groups of the periodic system.

Thus, for example, taking into consideration the fact that the formulas of the highest oxygen compounds formed by the elements of the second and third groups of the periodic system are EO and E_2O_3 respectively, it might be expected that the most typical compound of magnesium and boron would be the compound Mg_3B_2. It has recently been shown, however, that the compound in the Mg–B system containing least boron is apparently MgB_2. In the case of calcium a fairly stable compound CaB_6 is known. Countless other examples of such apparently unusual compounds could be shown. The fundamental ideas explaining the existence of such compounds were put forward by S. A. Shchukarev, who has shown that the composition assumed by thermodynamically stable compounds bear the stamp of the influence of the magnitudes of the enthalpies of atomization of the corresponding elementary substances.

In fact, each compound should be regarded as competing with the other compounds in the same system and with the elementary substances. In the light of this, S. A. Shchukarev has shown that, for example, the increase in the heats of atomization from chromium to molybdenum and on to tungsten corresponds to the disappearance of the lower forms of the oxides in the same direction (Cr_2O_3 is the most stable oxide of chromium, whereas Mo_2O_3 is thermodynamically unstable and W_2O_3 does not exist at all.) Expressed otherwise, in a number of cases there takes place an enrichment of the compound in the component characterized by the lower heat of atomization. This factor often apparently corresponds to the disappearance of a number of forms for compounds

*D. I. Mendeleev. Principles of Chemistry. Conclusion to the 1st edition 1871. (1945).

and thus explains the change in the thermodynamically stable compositions adopted by compounds, which is often observed on going from one element to another within a sub-group of the periodic system (this does not of course exhaust all the examples of these changes.)

The regularity pointed out above is observed, naturally, in the case where compound formation is accompanied by complete breakdown of the lattices of the separate elementary substances, i. e., when the lattices of the compound play practically no part in the bonds between the atoms of one and the same element in the total energy balance. Quite different relationships are observed in the case where the change in the character of the bond on going from the elementary substance to the compound, and the new structural conditions, do not hinder the preservation of various aggregates of the atoms of one or other of the elements in the lattice of the compound. In this case the lattice energy of the compound includes a more or less appreciable fraction of the lattice energy of the elementary substance. In this case, on the other hand, there is a corresponding tendency towards enrichment of the compound in the component with the higher value for the atomization energy, i. e., the conditions are established for the disappearance of the "normal" forms of the compound in favor of sub- and per-compounds.

Compounds corresponding to no single valence state are widespread, especially among the elements of the supplementary sub-groups. These include such compounds as, for example $VO_{2.17}$, $PrO_{1.83}$, $TiO_{1.67}$ etc. At the same time, in a number of cases, substances with such a somewhat unexpected composition prove to be the highest compounds in the corresponding systems ($ThS_{2.33}$, $ThSe_{2.33}$, $ThTe_{2.67}$).

It has recently been shown that, in the majority of cases, the composition of these mixed thermodynamically stable compounds is governed by a simple rule, namely, that the number of atoms of the element of the supplementary sub-group in one valence state is equal to twice the number of atoms of the element in the other valency state, i. e., the numbers are in the ratio 2:1.

There is every reason to suggest that the existence of this regularity is related to the fact that the ratio of the number of tetrahedral holes to the number of octahedral holes in the close-packed lattice of oxygen, sulfur, tellurium and other atoms, which forms the basis of the structure of the oxides, sulfides, tellurides etc., is also two to one.

The atoms of a particular element existing in different valence states are, of course, different particles, but since exchange of position may take place between the atoms with a corresponding change in their valence state but without a change in the energy of the lattice, they are to a certain extent equivalent, so that when the holes of both types in the lattice are filled to an equal extent, this should correspond to a maximum value for the entropy.

The question of the composition of compounds is directly linked to questions of the distance over which the compound extends on the composition axis and the sizes of their regions of homogeneity. It is well known that a deviation from the stoichiometric composition, even when the deviation is comparatively small, often leads to a marked change in physical properties, and, in particular, to the appearance of semiconductivity, which makes these substances interesting for practical purposes.

It is appropriate to point out in this connection that this property of binary compounds (of existing over a definite composition range) also changes regularly in the periodic system. It is necessary first of all to observe that a tendency to exhibit an appreciable region of homogeneity is, in the main, an attribute of compounds of the elements in the supplementary sub-groups (at any rate as far as compounds of a salt-like nature are concerned.)

At the same time we have to note a fairly well-defined tendency for the magnitude of the areas of homogeneity of analogous compounds to decrease as we move from top to bottom down a supplementary sub-group.

The question of the composition of binary compounds is closely connected with the question of their structures. It is known that definite areas of D. I. Mendeleev's table (studied in detail by G. B. Boky) correspond, as a rule, to definite types of structure for the lattices of the elementary substances or of their various compounds.

The Even-Number Rule

In the works of D. I. Mendeleev devoted in particular to the periodic law, there are to be found many extremely profound ideas, which at first did not attract the attention they deserved, and were later linked with the names of other scientists. A particular example of this is seen in the even-number rule, formulated by D. I. Mendeleev, according to which the elements of the even-numbered groups in the periodic system form for the most part compounds with even-numbered valences, while the elements in odd-numbered groups form chiefly

compounds with odd-numbered valences. From the point of view of contemporary theory, this is equivalent to the statement that stable compounds have no unpaired electrons not being used for chemical bonds. This rule, as is well known, has indeed been put forward by Lewis and is always introduced in association with his name, with no mention of D. I. Mendeleev.

It is well known that this rule of D. I. Mendeleev often explains the important reactions known as disproportionation and the disappearance of a compound of a particular composition in a whole series of systems. These disproportionation reactions are well known, i.e., $2TiCl_3 \rightarrow TiCl_2 + TiCl_4$; $2WCl_5 \rightarrow WCl_4 + WCl_6$ etc.

A study of the magnetic susceptibility as a function of temperature for certain compounds has shown that ordinary disproportionation, which appears as decomposition into two phases, is sometimes preceded by a phenomenon which may be called "internal disproportionation." For example, Klemm has shown that when $TiCl_3$ is heated to a temperature of approximately 300°, at which the formation of the new phases $TiCl_2$ and $TiCl_4$ has not yet taken place, a value is obtained for the magnetic susceptibility which is close to that which would be obtained if in the $TiCl_3$ lattice a process had taken place by which two atoms of trivalent titanium had been converted into an atom of divalent and an atom of tetravalent titanium: $2Ti^{+3} \rightarrow Ti^{+2} + Ti^{+4}$.

According to our preliminary data, the oxide $VO_{2.17}$ at fairly high temperatures contains not tetravalent and pentavalent vanadium, as might be supposed, but trivalent and pentavalent vanadium, again in full agreement with the rule enunciated by D. I. Mendeleev.

SUMMARY

We have reviewed above certain phenomena in which the periodic laws and other principles formulated by D. I. Mendeleev are most clearly illustrated.

It is well known, however, that other regularities governing the chemistry of more complex compounds are also covered by the periodic law.

In this connection it is necessary to mention the works of I. I. Chernyaev and A. A. Greenberg concerning an important field of inorganic chemistry – the chemistry of the complex compounds.

It is well known that the ever-widening researches of contemporary technology demand the preparation of substances with a definite set of properties. Examples are semi-conducting materials, metallic alloys with definite mechanical and other properties, materials resistant to high temperatures and many others. In spite of the developments which are taking place at an ever-increasing rate in the theory of the chemical bond and in the theories dealing with the connection between the physical properties of chemical compounds and their composition, these ideas are far from being at a stage of completion which could enable us at the present time to rely on them for the purpose of making accurate predictions.

The periodic system may serve successfully as a guide in such research. It is well known, for example, that elementary substances characterized by semiconductivity are found in a particular region of the periodic system, namely, the central part.

It should be noted that at the present time two aspects of the periodic system are developing: one concerned with the electron clouds, which is directly linked with the chemical properties of the elementary substances, and the other, the nuclear aspect. Without going into a detailed examination of the nuclear aspect, we would only note that the work of the past ten years has also established a periodicity in the nuclei of the atoms. An example of this periodicity is provided by the periodicity in the distribution of the chemical elements in nature, the study of which owes much to the work of V. I. Vernadsky, A. E. Fersman and A. P. Vinogradov.

It is appropriate to mention that the existence of levels in the structure of the atomic nucleus was first noted by S. A. Shchukarev and P. N. Selinov, who, in their studies, have also adopted the method of comparative research and generalization of experimental facts, which led D. I. Mendeleev to his immortal discovery.

Received January 17, 1957

Leningrad State University

PROBLEMS OF CHEMICAL STRUCTURE IN THE WORKS OF D. I. MENDELEEV

V. V. Razumovsky

The ideas and work of D. I. Mendeleev initiated a long series of new developments in the scientific principles of chemistry and produced revolutionary changes in the development of theories of the atom and molecules. D. I. Mendeleev has played an outstanding part in solving the most important problems of chemical structure.

In 1856, in his dissertation for the master's degree "Specific volumes," when ". . . the very distinction between particles and atoms was obscure and was being constantly confused in scientific language," Mendeleev made a strict logical enunciation of the principles of molecular theory ([1], pp. 140-317; [2], pp. 112-228). In 1858-1859, when delivering a course in organic chemistry in Peterburg university, he laid the full basis for the concept of the molecule [3]. In 1861, in the first edition of his text-book "Organic Chemistry," Mendeleev wrote:

"Consequently, the most simple formulae, expressing only the elementary composition, are insufficient, and the proportional weights corresponding to these formulae do not satisfy the requirements and the aims of science. For their satisfaction, the concept of the chemical particle (molecule) is required. A particle of a substance is the amount which enters into a reaction.

". . .Since the concept of the particle forms the basis of all the conclusions of this system, it seems to me to to be more convenient to refer to it as particulate (molecular)" ([4], p. 45).

In pointing out the importance of the concept of the molecule in the development of chemical science, Mendeleev says: "When the above concept of the molecule is accepted, many regular relationships in the physical properties of substances are observed, the system is perfected, and not only are a large number of reactions explained and generalized, but a strict classification of them is obtained and many new reactions can be accurately predicted. The student of general and special fields of organic chemistry will see at every step the fertility of the accepted concept of the particle"([4], p. 45).

As early as the fifties of the last century, Mendeleev confirmed and developed the ideas of Avogadro. Using Avogadro's law as a basis, he derived a formula for the determination of the molecular weight of gaseous substances from the density of the gaseous substances relative to air ([1], pp. 185-193, 316). Mendeleev pointed out that the deviations of some gaseous substances from Avogadro's law are only apparent, since they are the result of the thermal dissociation of these substances. He wrote: "Evidence for the probability of all these dissociations, confirmed by analogy and by the specific volumes, is provided by: 1) the possibility of the existence of all the products of the system in an isolated state; 2) the approach of the specific volumes of these substances to the true sum of the volume of the components as the temperature is raised and complete decomposition takes place, as has been shown by the studies of Cahour on phosphorus pentachloride, whose volume, according to Mitscherlich's work (at 185°), is equal to 3. In the case of sulfuric acid, complete dissociation has not taken place at the temperature at which Bineau's studies were carried out, so that its specific volume is equal to 3, and not 4; 3) the actual, experimentally confirmed decomposition of PCl_5 into PCl_3 and Cl_2; 4) the low stability of all 9 substances mentioned; 5) the onset of further dissociation in those cases where the products formed are themselves unstable. . . Of course, for all the substances except PCl_5, this is only one probable explanation for the volume occupied by their vapors and is still open to doubt until it has been confirmed by experiment; but the likelihood of this suggestion has been confirmed in almost 200 cases by the good agreement between the equivalents, the basicity and the double volume of the particles of the substances" ([1], p. 190).

It should be noted that at this time and even in later years A. Kekule considered the concept of the molecule to be hypothetical. In his "Text-book of Organic Chemistry" in the first (1861) and second (1867) editions he wrote: "Since the causes lying at the basis of this empirical law (the law of Avogadro–Ampere, –V.R.) have not yet been established with complete certainty, it is clear that this law does not yet have that degree of reliability which is characteristic of the laws of nature" [5].

Kekule denied the objective reality of atoms and molecules, considering them as mere symbols created for convenient classification of chemical phenomena: "Since conclusions regarding the atomic weights of elements, and the molecular weights and constitution of molecules, can be only speculative, it is clear that in the course of the development of science they should be constantly changing, that they are even now constantly changing, and that at one particular time, different chemists may hold different views" ([5b], p. 59).

In developing the study of the composition of chemical compounds and the theory of saturation, Mendeleev came to the conclusion that any two parts of one and the same molecule are equivalent to one another and are therefore capable of replacing one another. He considered that chemical compounds had saturated – energetically stable – and unsaturated – energetically unstable– compositions. In the case of the hydrocarbons the saturated composition is that of the paraffins, whose molecular composition is expressed by the general formula C_nH_{2n+2}. The distinguishing feature of hydrocarbons which are not saturated is their ability to undergo direct combination with various substances.

Chemical compounds which are not saturated are related to different stages of saturation of the valences of the atoms. The ethylenic hydrocarbons represent the first stage relative to the paraffins. The second stage is represented by the hydrocarbons C_nH_{2n-2}, the third by C_nH_{2n-4} and finally the fourth by the aromatic hydrocarbons C_nH_{2n-6} ([4], pp. 23, 456).

According to Mendeleev, ". . .all organic compounds are grouped round the hydrocarbons" ([4], p. 460).

Starting from the idea that the methyl group is capable of a separate existence and is able to replace hydrogen, Mendeleev introduces the homologous series of saturated hydrocarbons, beginning at the methane molecule. He introduces the homologous series of saturated alcohols by substituting an equivalent hydroxyl group for a hydrogen atom in the molecules of the corresponding hydrocarbons. In exactly the same way he introduces homologous series of other organic compounds.

Mendeleev understood that the study of homology could not embrace all the varied phenomena of organic chemistry: "The conception of homologous series of saturated and unsaturated hydrocarbons, which serves to simplify and explain a large number of facts, is not, however, so general that it is able to explain all the facts related to organic compounds" ([2], p. 342).

Recognizing the fundamental principles of the theory of chemical structure, he said, in lectures delivered in 1868 in the Peterburg Technological Institute: "We shall present a short form of the hypothesis which is being accepted by many chemists at the present time and which provides a simple explanation of all the phenomena of organic chemistry. This hypothesis is based on the formulation of two postulates: 1) that carbon is a tetraatomic element. This proposition follows from a comparison of carbon with chlorine or hydrogen . . . In order to create a picture of how we can have compounds with 2, 3 etc. parts of carbon, let us imagine that carbon has a known number (4) of planes of affinity, a known number of affinities or equivalents of affinity, with which it attracts elements. This is the first postulate. 2) The second postulate refers only to organic compounds and supposes that if a certain element holds other elements by means of its affinities, then it is also able to hold to itself. For example, if carbon is capable of holding hydrogen, then it is also capable of holding carbon. From this hypothesis the ideas of the composition and properties of organic compounds readily follow" ([2], p. 342).

Mendeleev's studies in the field of solution chemistry were of great importance in understanding the nature of substances and discrete forms of matter. His study of solutions led Mendeleev in 1864 to suggest that there is no boundary between definite and indefinite chemical compounds. "Indefinite chemical compounds [stated the great chemist] for example, solutions, cannot be sharply distinguished from definite ones, or the so-called true chemical compounds "([6], p. 151).

Mendeleev's studies on chemical compounds of indefinite composition and his discovery of the hydrates of sulfuric acid and ethyl alcohol led to a radical revision of the views on the nature of solutions generally accepted at that time.

Mendeleev's work established that the process of dissolution is a chemical process. The formation of hydrates of definite composition in sulfuric acid solutions and aqueous solutions of alcohol provided irrefutable proof of the existence of chemical interaction between the component parts of the solution.

"An examination of all the facts known at the present time [writes Mendeleev] concerning indefinite chemical compounds, leads me to the conviction that definite chemical compounds are only a particular case of indefinite chemical compounds, and that a fuller study of the latter will have an influence on the theoretical views concerning the whole of chemical knowledge" ([6], pp. 2, 220). The views of V. V. Markovnikov in the period 1865-1867, concerning the absence of a boundary between definite and indefinite chemical compounds, are very close to the theoretical ideas of Mendeleev [7, 8].

In the further development of his ideas concerning the nature of indefinite chemical compounds, Mendeleev points out the very varied character of the interactions between their component parts and the variability of these interactions. By a comparison of chemical compounds undergoing dissociation with molecular compounds, he establishes that they differ only in their ability to decompose into their component parts. These ideas led Mendeleev to regard solutions ". . .as liquid, unstable, definite chemical compounds undergoing dissociation" ([6], pp. 460, 523). Having established the reversibility of the processes of dissociation and association in solutions, Mendeleev discovered their dynamic character: "The solvent particles, found at one moment in the compound, may be liberated the next moment, only to enter again into concordant movement with the particles of the solute" ([9], P. XI). All his studies were governed by the idea ". . . of determining the chemical structure of solutions" ([9], p. 20).

Mendeleev categorically rejected static concepts in the science of solutions. He maintained that the complex interactions taking place in solutions could only be understood and explained on the basis of dynamic principles: "My concept of solutions is dynamic, and I do not agree with the prevailing static ideas ([9], p. 20). Mendeleev also proved that there is likewise no sharp boundary between definite chemical compounds and molecular compounds ([6], p. 269).

Subsequently A. M. Butlerov also accepted the absence of sharp boundaries between ordinary chemical compounds, molecular compounds and solutions. He said: . . ."we have absolutely no criteria for a strict distinction between a chemical particle and a compound formed between particles; the change from the latter to solutions etc. is also quite gradual and unnoticeable. Here, as everywhere, distinctions and classifications belong not to nature, not to the true state of affairs, but to human opinion, which requires them for its own convenience" [10].

Mendeleev considered that molecular compounds could consist of a number of molecules and thus rejected the prevailing ideas according to which molecular compounds were taken to be formed by two particles. At the same time he pointed out that in molecular compounds ". . .the position of the attached particles relative to the particle to which they are attached is of great importance" ([6], p. 269). Mendeleev likewise did not agree with the deeply-rooted idea that a molecular compound was a simple mixture of particles. From his point of view, when an odd number of attached particles was present, one of the particles occupied a special position in the molecular compound and in this way acquired specific properties: ". . .in this case [says Mendeleev] we obtain not a simple mixture of the particles, but the particles formed acquire a special type of movement, which accounts for its different properties" ([6], p. 269). From this standpoint Mendeleev came to a criticism of S. Arrhenius's electrolytic dissociation theory. Mendeleev categorically rejected the main postulate of Arrhenius's theory of the dissociation of the molecules of electrolytes in solutions into free ions. In his "Principles of Chemistry" he wrote: ". . . in the process of dissolution, it is most probable to suppose the formation of new, extremely complex, but unstable and readily decomposing dissociating compounds, and not the breaking down, even in part, of the substance taken" ([6], p. 543).

Mendeleev saw the reason for the electrical conductivity of solutions as the combination of the dissolved substance with the solvent: ". . . the best conductors of current are solutions, such as those of sulfuric acid, in which we have to admit the formation of associated systems or hydrates" ([6], p. 543). At the present time Mendeleev's ideas concerning the nature of electrolyte solutions are generally accepted and have found expression in studies of ion solvation and hydration.

The recognition of the arbitrariness and variability of the boundaries between definite and indefinite chemical compounds led Mendeleev to a most important generalization for the dialectical understanding of phenomena

in nature and in technology, namely the conclusion that there is no sharp distinction between acids and bases: ". . . For us there is no sharp distinction between a metal and a metalloid, between an acid and a base" ([11], p. 98).

These generalizations of Mendeleev, which embrace the results of a vast number of experimental studies by many generations of scientists, have led to the recognition of the interaction between all the atoms in particles and between the particles in high-molecular compounds and in solutions. They have disclosed the unity of the contrasting aspects and properties of the chemical elements, acids and bases, and definite and indefinite chemical compounds. They have shown that, in every chemical element and in every chemical compound, contrasting properties are mixed in a definite proportion. They have established that the accepted division of the chemical elements and chemical compounds according to the contrast and differences between them is not absolute but only relative. By developing and extending his ideas on the arbitrariness and relativity of boundaries in nature, Mendeleev arrives at the postulate that there is no ground for a division of phenomena into two classes – physical and chemical. "The term 'physical processes' is now used to describe those processes [writes Mendeleev] which are accompanied by a rearrangement of the particles themselves, but not by a change in their structure. But in this case there are no physical processes, since all the phenomena of heating, fusion etc. result from a change in the particles and are consequently chemical changes.

The fact that physical processes do actually affect the particle itself may be convincingly seen from the fact that substances decompose under the influence of high temperature. In short, there are no grounds for dividing all processes into two types – physical and chemical" (my italics, – V. R.) ([6], pp 266-267).

Taking a stand against the concept of indivisible and unchanging atoms, Mendeleev, in the first edition of "Principles of Chemistry" (1871), develops materialistic ideas concerning the complexity and divisibility of atoms: ". . . the atoms of elementary substances are essentially complex bodies formed by the coalescence of still smaller parts (ultimates); that which we describe as indivisible (the atom) is indivisible only by normal chemical forces, just as particles are indivisible in ordinary conditions by physical forces; however, in spite of the arbitrariness and novelty of this suggestion, the mind is unwittingly drawn towards it on acquaintance with chemistry" ([12], p 805). Mendeleev emphasized that "indivisible"atoms are "further divisible by a number of methods."

Mendeleev's atomic theory is permeated by the idea of the indissoluble link between matter and motion and the establishment of the unity between the microcosm and the macrocosm. In establishing relationships between the atoms – the individual units of the microcosm – and the sun and planets – the individual units of the macrocosm, Mendeleev writes: "But the invisible world of chemical changes is fully comparable to the visible world of the heavenly bodies, because our atoms are the individual units of the invisible world, comparable to the planets, satellites and comets of the astronomers, and our particles are comparable to such systems as the solar system or the systems of the double stars. Ammonia (NH_3) can be most simply pictured as containing nitrogen as its sun and hydrogen as its planets, while ordinary salt (NaCl) may be pictured as a double star formed by sodium and chlorine" ([4], p 638).

Further development of the ideas of Mendeleev led V. Ya. Kurbatov to the concept of the complex structure and divisibility of the electron: "Let us take D. I. Mendeleev's teaching a little further. At the present time two ultimate categories of individual unit are known: the lower limit of divisibility – the electrons – and the upper limit – the systems of the stars. But there is no reason to suppose that there cannot exist individual units consisting of systems of the stars, just as the latter consist of solar systems. In the same way it should not be thought that electrons represent the limit of divisibility. If the world is infinite, then electrons are divisible" [13].

In the past two decades a number of elementary particles have been discovered, and the preliminary data obtained indicate that these are of complex structure, which provides thorough experimental proof of the suggestion put forward by Mendeleev.

The saturation theory enunciated by Mendeleev was a further development of the unitary theory (theory of types) of Gerhardt. This however did not prevent Mendeleev from exposing the weak points in the unitary theory. At the basis of Gerhardt's unitary ideas lay a postulate denying the possibility of obtaining a knowledge of the nature of matter and the internal structure of molecules. The unitary theory classified all chemical compounds into four types and left the question of other possible types quite open. It did not reveal the reasons for the typical properties of the chemical compounds and did not show the predominance of such types as those of ammonia,

water, hydrogen and hydrogen chloride over other types. All chemical reactions in the Gerhardt theory were limited to double decomposition reactions, and this in itself created quite inaccurate ideas concerning the ways in which chemical compounds were formed.

In an analysis of the fundamental principles of the unitary theory (the theory of types), Mendeleev pointed out: "All the principles of the Gerhardt system which we have presented are, without doubt, far from being science's last word on the subject, but this is, at least, the highest level attainable by us at the present time" ([1], p 167). He later wrote: "Gerhardt, who has contributed so much to the development of accurate concepts in contemporary chemistry and who has spread with such success the concept of substitution, has, in my opinion, gone too far and sees substitution in all reactions " ([2], p 150).

At the same time Mendeleev produced a critical study of atomicity, since this theory suggested a static concept of atoms and molecules. He decisively rejected the idea of a constant atomicity for the elements such as was held and defended by Frankland, Kekule and their successors.

As a result of a deep and comprehensive analysis of the theory of the atomicity of the elements in the light of the periodic law, Mendeleev came to the following conclusions:

"1) This theory relies on and cannot do without the division of all chemical compounds into two classes – atomic and molecular. It deals with only the former and pays no attention to a discussion of the latter. This division, which, it is true, has prevailed for a long time, has no justification; it is arbitrary and artificial. . . .

"2) The starting point for a discussion of the atomicity of the elements is provided by the hydrogen compounds, but of the 63 elements, not more than 17 have up to the present [time] been found to combine with hydrogen; at the same time, there is formed only one compound with one atom of the element, whereas other elements, even chlorine, are capable of forming several compounds, so that to judge compounds with other elements according to the hydrogen compounds, is, to say the least, very impracticable. Even carbon forms only CH_4 with hydrogen, and not CH_2, whereas with oxygen it gives both CO_2 and CO. The existence of particles $SnCl_2$ and $SnCl_4$, HgCl and $HgCl_2$, PCl_3 and PCl_5 etc. provides constant difficulties for the supporters of the theory of the atomicity of the elements precisely because they start with the hydrogen compounds, which exist in only one form.

"3) All elements except fluorine combine with oxygen, oxygen compounds predominate in nature and are extremely clearly distinguishable in chemical character, many elements give a number of compounds with oxygen, yet the theory of the atomicity of the elements gives no laws for determining the number of atoms of combined oxygen, because it is considered to be diatomic and capable of reacting with every closed particle. . .

"4) The most consistent of the supporters of the theory under consideration are those who consider the atomicity to be a fundamental and therefore constant property of the atoms. In this connection it is often stated that there are no free affinities in the particle. They consider that carbon is always tetra-atomic, nitrogen always triatomic, etc. But even they have to admit the facts, and the majority today consider atomicity as a variable property of the elements. In effect, once the variability of atomicity is admitted, atomicity itself is rejected; it becomes no more than the question of the number of equivalents contained in the atom: since the equivalent of an element changes according to the law of multiple proportions, the atomicity also varies . . . When variability, free affinities and latent atomicity are once admitted, the theory has begun to break down, because the logical consistency of the theory is shaken and the fundamental postulates of the theory have lost ground" ([2], p 304).

In rejecting constant atomicity in the chemical elements, and the unchangeable and static character of atoms, Mendeleev pointed to the interaction between all the atoms present in the molecule and to the variation in their structure and properties resulting from intermolecular reactions.

Mendeleev's work established the complete bankruptcy of those theoretical concepts in chemistry which regarded the molecule as the sum of its component parts and denied the possibility of interaction and mutual influence between the constituent atoms.

As early as 1865, in his dissertation for the doctorate "A Discussion of the Compounds formed by Alcchol and Water," Mendeleev wrote: "The varying character of hydrogen in its compounds depends first of all on the elements to which it is combined" ([6], p 151). In a further study of the mutual relationship between the parts of the molecule and the whole, Mendeleev (1870) came to the conclusion that ". . . the atoms which come together in solid and liquid bodies influence one another, there can be no doubt, not only by virtue of their total

mass (the whole weight of the particle) but also by virtue of their parts (i.e., by virtue of the separate atoms constituting the particle and the parts of the atoms themselves). . ." ([12], p 199).

In the article "Periodic Laws governing the Chemical Elements," (1871) there is given the most complete and comprehensive exposition of the importance of the periodic law in the study of the structure and properties of chemical compounds. "Atoms and particles [writes Mendeleev] should be pictured as existing in a sort of mobile equilibrium and undergoing interaction with one another. The whole system is bound together by the forces belonging to the separate parts, and it cannot be imagined that a particular two parts of the whole are dependent upon a third part without influencing one another, particularly when all that we know concerning these two parts points to a clear and constant interaction between them" ([11], p 209; [2], p 297). With his deep understanding of the existence of the mutual influence between atoms, Mendeleev saw the reason for this influence in the complexity of the structure of the atom, and pointed out the influence "of the parts of the atoms themselves." He recognized the universal interaction of the atoms in particles: "While it is accepted that in CH_4 the carbon provides the only link between the hydrogen atoms, there is nothing surprising in this, but when one hydrogen is replaced by chlorine, then it does appear surprising since it cannot be thought that the chlorine has no influence on the hydrogen, or that the carbon alone remains the only connection between the hydrogen and the chlorine, or that the attraction between H and Cl plays no part either during the reaction or afterwards" ([2], p 297). Mendeleev related the properties of molecules not only to the nature and number of the atoms of the elements composing them, but also to their structure: "The properties of particles (substances) depend not only on the properties of the elements present (and consequently not only on the atomic weights of the elements present), and not only on their number, but also on their structure and the forms in which each element enters the particle" [14]. This idea of D. I. Mendeleev has been provided with a firm justification by contemporary theory of the structure of the electron clouds in atoms.

He closely related the properties and reactions of molecules, and the intramolecular reactions of atoms, to the conditions in the surrounding medium: ". . . it must be recognized that both particulate and atomic movements change, in the same way as the physical states, with changing conditions: temperature, pressure and electrical tension" ([15], p 347).

In asserting the existence of chemical interaction and mutual influence between the component parts of the molecule and the whole, Mendeleev arrived at a rejection of the principle of additivity in chemistry. With a vast amount of accumulated experimental data, he showed the lack of evidence for the principle of additivity in relation to specific volume. As early as 1856, in his dissertation for the master's degree, "Specific Volumes," Mendeleev showed clearly that the volume of the component parts of a chemical compound cannot be estimated from the volume of the whole compound. In "Postulates chosen for Defence of the Master's Degree in Chemistry," he emphasized: "The efforts of Schreder, Gmelin, Grosshantz and Dana to get the specific volumes of solid and liquid substances to agree with the number of parts are as yet quite unsuccessful" ([1], p 316).Later (1871), taking the specific volumes of chlorine compounds as an example, he established the absence of additivity in the volumes of the chlorine compounds relative to the volumes of their constituent elements ([16], pp 545-557).

In chemistry lectures in the teaching session 1870-1871, Mendeleev stated directly that ". . .the volume of a chemical compound is not equal to the sum of the volumes of the materials of which it is composed, and it would be a serious mistake to picture a chemical compound as a mechanical union of atoms in space, each of which always preserved in this union a constant definite volume" ([16],p 261).

Mendeleev rejected the static approach to the internal structure of matter and considered that atoms and molecules are in a state of continual movement: "On witnessing the reserve of vital force shown in atoms and particles in the process of their interaction, and giving rise to the physical and mechanical phenomena which accompany them, chemists must recognize in the particles themselves, atoms in motion, possessed of a vital force which cannot be created or destroyed, like matter itself. In chemistry, therefore, we must recognize and seek out mobile equilibria not only between particles, but also within them, between the atoms ([4], pp 638-639). According to Mendeleev's view, the molecules of a substance, even when not taking part in chemical reactions and changes, were in a state of continual movement and change: ". . . when there is no chemical change, when substances are remaining unaltered, there is still taking place this motion, which undoubtedly constitutes chemical dynamics" ([15], p 446).Mendeleev established the reversibility of chemical reactions and changes. "If only, [he wrote] we acquaint ourselves with chemical relationships, then we are finally convinced that chemical reactions or relationships are reversible" ([15], p 569). He called for the discovery and study of the conditions

ot the mobile equilibria between molecules and within them. He considered that " . . . chemical phenomena of all types result, of course, from the reorganization of these internal movements, of the nature of which little is yet known, but which must be recognized in the light of the total present-day knowledge of the movement which prevails everywhere in nature" ([4], pp 642-645). Mendeleev understood that the chemical changes undergone by molecules resulted from intermolecular movements and rearrangements of the atoms, leading to a change in the state of the material.

Mendeleev also discussed the nature of the motion of the atoms in molecules. He considered that the atoms in molecules were moving in elliptical orbits around one definite atom, "around its center of motion." A change in the conditions of the outer surrounding medium, in Mendeleev's opinion, was reflected in a change in "these ecliptics." He related the phenomena of isomerism and dissociation in molecules to a change in the form of the elliptical orbits of the atoms and to their relative inclination ([6], p 267).

Mendeleev's work showed quite clearly that static models of atoms and molecules give only a rough and incomplete picture of matter in its state of constant movement and change. His development of atomic and molecular theory led Mendeleev not only to the establishment of mutual connections and mutual transfer between chemical elements, but also to the discovery of the dynamic nature of atoms and molecules, of the mutual intramolecular influence of atoms, and of the reversibility of chemical reactions and changes. The Mendeleevian principles of atomic and molecular theory showed that the chemical form of the motion of matter was related to the qualitative changes in the structure of matter and to the mutual interconversion of the particles of matter. The ideas and principles put forward by Mendeleev form the principal basis for the construction of a dynamic theory of chemical processes.

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INVESTIGATION OF THE $Co(ClO_4)_2$–Li_2–(H_2O)–ACETONE SYSTEM BY PHYSICO-CHEMICAL ANALYSIS METHODS

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The system studied, which consists of two salts with different ions and solvents in which a double exchange reaction is possible, is a quaternary system. For a geometric representation of the equilibria in this system one may use a right pyramid with a square base, with the salts $Co(ClO_4)_2$, $CoBr_2$, $(LiClO_4)_2$ at the corners and the solvent at the apex. The amount of water in this system was determined by the water content of the crystalline hydrate $Co(ClO_4)_2 \cdot 6H_2O$, as the preparation of anhydrous cobaltous perchlorate was unsuccessful – on heating in vacuum cobaltous perchlorate decomposes.

In this report we present the results of investigating sections of the $Co(ClO_4)_2$–Li_2Br_2–H_2O–acetone system, in which we found reactions between the salts. Physical chemical analysis shows that definite conclusions on the nature of the interaction of the components in a system can only be based on a study of a combination of properties [1].

In this particular system we studied the light absorption, electrical conductivity, density and viscosity of the solutions. Data on the density was used to calculate the viscosity of the solutions.

EXPERIMENTAL

Cobaltous $Co(ClO_4)_2 \cdot 6H_2O$ and lithium perchlorates $LiClO_4 \cdot 3H_2O$ were prepared from the carbonates (analytically pure) and perchloric acid (specially pure), as we described previously [2]. Cobaltous $CoBr_2 \cdot 6H_2O$ and lithium bromides $LiBr \cdot H_2O$ were prepared from the carbonates (analytically pure) and hydrobromic acid (analytically pure) with two subsequent recrystallizations. After two recrystallizations, $LiBr \cdot H_2O$ was dried at 100° [3]. The acetone (analytically pure) was dried with calcium chloride and distilled twice. It was tested as described in the literature [4].

The solution concentrations are expressed in molar percentages. The methods of preparing the solutions and measuring the light absorption, electrical conductivities, viscosities and densities of the solutions, we described previously [2].

The optical density isotherms of the solutions given in this paper, refer to the wavelengths where the characteristic points appear most clearly. We used freshly prepared solutions for the experiments.

The $Co(ClO_4)_2$–Li_2Br_2–(H_2O – acetone system (0.12 mole% total salts). An acetone solution of cobaltous perchlorate and also a solution of lithium bromide do not absorb in the part of the spectrum investigated. Light absorption in this system depends on the formation of cobaltobromide compounds.

The optical density isotherms at the wavelengths 600, 675, 710 and 715 mμ and d=1.00 mm are given in Fig. 1. At a wavelength of 600 mμ, a maximum is observed, the abscissa of which corresponds to a ratio $Co(ClO_4)$: Li_2Br_2 =1:1.

The formation of the compound, corresponding to this maximum, may be represented by a double exchange reaction

$$Co(ClO_4)_2 + Li_2Br_2 = CoBr_2 + 2LiClO_4.$$

At a wavelength of 675 mμ the optical density isotherm consists of two parts, intersecting in a maximum, the abscissa of which corresponds to a ratio $Co(ClO_4)_2:Li_2Br_2=2:3$, indicating the formation of the compound $CoBr_2 \cdot LiBr$ in the system. At 715 mμ a maximum is observed, the abscissa of which corresponds to the ratio $Co(ClO_4)_2:Li_2Br_2=1:2$, indicating the formation of the compound $CoBr_2 \cdot 2LiBr$.

Thus, the optical density isotherms of this system in various parts of the spectrum show the presence of the compounds: $CoBr_2$, $CoBr_2 \cdot LiBr$, $CoBr_2 \cdot 2LiBr$. The $CoBr_2$ is detected at a wavelength of 600 mμ, the compound $CoBr_2 \cdot LiBr$ is observed in the region of the spectrum from 665 to 705 mμ, and the compound $CoBr_2 \cdot 2LiBr$ is detected in the long-wave part of the spectrum in the region of 710–720 mμ.

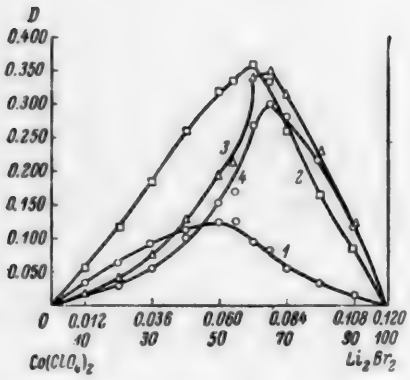

Fig. 1. Optical density (D) of the $Co(ClO_4)_2$ –Li_2Br_2–(H_2O)–acetone system. Total salts 0.12 mole %, thickness of layer 1.00 mm. Wavelength (in mμ):1–600, 2–675, 3–710 4–715.

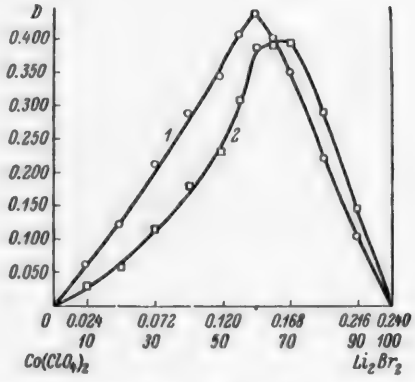

Fig. 2. Optical density (D) of the $Co(ClO_4)_2$ –Li_2Br_2–(H_2O)– acetone system. Total salts 0.24 mole %, thickness of layer 0.52 mm. Wavelength (in mμ): 1–680, 2–710.

In order to follow the effect of changing equilibrium factors on the position of the maxima, observed on the optical density isotherms, we studied the section $\sum[Co(ClO_4)_2+Li_2Br_2]$ =0.24 mole%, (H_2O–1.44 mole %), acetone – 98.32 mole %.

The optical density isotherms of the solutions at 680 and 710 mμ and d=0.52 mm are given in Fig. 2. These confirm the formation of the compounds $CoBr_2 \cdot LiBr$ and $CoBr_2 \cdot 2LiBr$ in the system.

Studying the electrical conductivity and viscosity of the system showed that the electrical conductivity – composition and $\kappa\eta$ – composition curves confirmed the formation of only one of the complex cobaltobromide compounds (κ – electrical conductivity, η – viscosity of the solutions). As the κ – composition and $\kappa\eta$ – composition curves are completely identical, we show only the $\kappa\eta$ – composition curve here. In Fig. 3, we give the $\kappa\eta$ – composition curves for the sections with 0.12 and 0.24 mole % total salts at 25 and 40°. Each of the $\kappa\eta$ – composition curves given consists of two parts intersecting in a maximum, the abscissa of which corresponds to a ratio $Co(ClO_4)_2:Li_2Br_2=2:3$, confirming the formation of the compound $CoBr_2 \cdot LiBr$, in the system. Consequently the characteristic points, observed on the electrical conductivity – composition and $\kappa\eta$ – composition curves, do not change their abscissae (composition) on changing the solution concentrations and temperatures.

Comparison of the light absorption – composition, electrical conductivity – composition and $\kappa\eta$ – composition diagrams we studied, shows that the formation of the compound $CoBr_2 \cdot LiBr$ in this system is observed on the optical density, electrical conductivity and $\kappa\eta$ isotherms.

The $CoBr_2$–Li_2Br_2–(H_2O)– acetone system (0.12 mole % total salts, 0.72 mole % H_2O and 99.16 mole % acetone). Acetone solutions of cobaltous bromide, like acetone solutions of cobaltous chloride, have a blue color, even at low concentrations.

The light absorption of a 0.2 M acetone solution of cobaltous bromide and also the light absorption of a 0.099 M acetone solution of cobaltous bromide in the presence of a 0.2 M solution of lithium bromide was studied by Dirking [5]. As studying the light absorption shows, cobaltobromide compounds of different degrees of complexity are present in acetone solutions of cobaltous bromide.

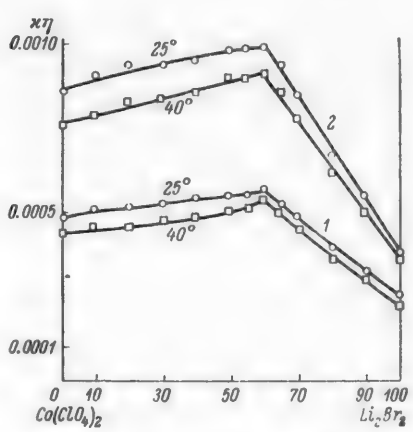

Fig. 3. Electrical conductivity, corrected for viscosity, of the $Co(ClO_4)_2$–Li_2Br_2–(H_2O)–acetone system. Total salts (mole %): 1–0.12, 2–0.24.

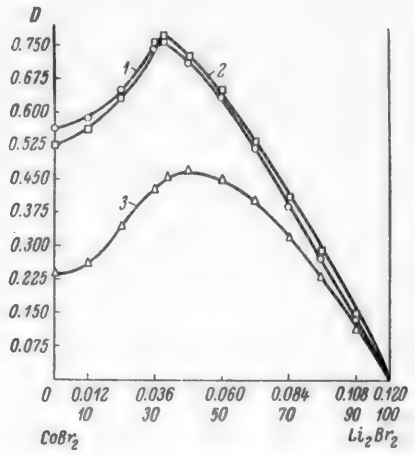

Fig. 4. Optical density (D) of the $CoBr_2$–Li_2Br_2–(H_2O)–acetone system. Total salts 0.12 mole %, thickness of layer 1 mm. Wavelength (in mμ): 1–690, 2–695, 3–715.

However, in addition to them, solvated divalent cobalt cations are also present and this causes absorption in the region of 505 mμ in acetone solutions of cobaltous bromide. The presence of solvated divalent cobalt cations in acetone solutions, together with complex cobaltobromide compounds, is also confirmed by observations on ion transport in an electrical current. On passing an electrical current through an acetone solution of cobaltous bromide, one observes transport of cobalt to the anode as complex cobaltobromide anions and to the cathode in the form of solvated divalent cobalt cations [5].

The addition of lithium bromide to an acetone solution of cobaltous bromide displaces the equilibrium towards the formation of complex cobaltobromide compounds and also contributes to the displacement of solvent molecules from the solvate capsules of the complex cobaltobromide compounds. Hence, on adding lithium bromide, these processes are reflected in the absorption band in the region of 600 – 700 mμ, observed in acetone solutions of cobaltous bromide and caused by the presence of complex cobaltobromide compounds in the solution, being displaced towards the long wave part of the spectrum, i. e., into the region of the spectrum where cobaltous bromide absorbs in concentrated HBr solution. In a solution in which the ratio $CoBr_2$: HBr=1:2310, practically all the cobalt ions form complex cobaltobromide compounds and absorption in the 500–517 mμ region of the spectrum, characteristic of divalent cobalt ions, is not observed [6].

The study of the light absorption of a 0.099 M acetone solution of cobaltous bromide in the presence of a 0.2 M solution of lithium bromide, carried out by Dirking [5], did not lead to the determination of the composition of the complex cobaltobromide compounds in the solution. Only their presence was established: the appearance of absorption bands in the 600–700 mμ region of the spectrum was caused by the presence of a new electronic system, belonging to the complex cobaltobromide compounds.

Light absorption of the section studied for the $CoBr_2$–Li_2Br_2–(H_2O)–acetone system was measured in the 600–740 mμ region of the spectrum, in which the complex cobaltobromide compounds absorb, as the above work shows. The optical density values of the solutions, which we obtained for this section, are given in Fig. 4. The optical density isotherms at wavelengths of 690 and 695 mμ and d = 1.00 mm consist of two parts intersecting in a maximum, the abscissa of which corresponds to a ratio $CoBr_2$: Li_2Br_2 = 2:1.

The formation of this compound in the system may be represented by the equation $2CoBr_2 + Li_2Br_2 = 2(CoBr_2 \cdot LiBr)$. In order to determine if the abscissa (composition) of this characteristic point would change on changing equilibrium factors, we also investigated a section of this system with 0.24 mole % total salts and 98.32 mole % acetone content. Data on optical density measurements on the solutions are given in Fig. 5. On the optical density isotherms at wavelengths of 685 and 695 mμ and d = 0.52 mm there are maxima, whose abscissae correspond to the ratio $CoBr_2:Li_2Br_2 = 2:1$. Thus, on changing the solution concentrations the abscissa of the characteristic point on the optical density – composition curves remains constant.

To determine if the characteristic point observed on the optical density isotherms would appear on the isotherms of other properties, we studied the electrical conductivity and viscosity of sections with 0.12 and 0.24 mole % total salts at 25 and 40°. The results of the electrical conductivity measurements, corrected for viscosity, are given in Fig. 6.

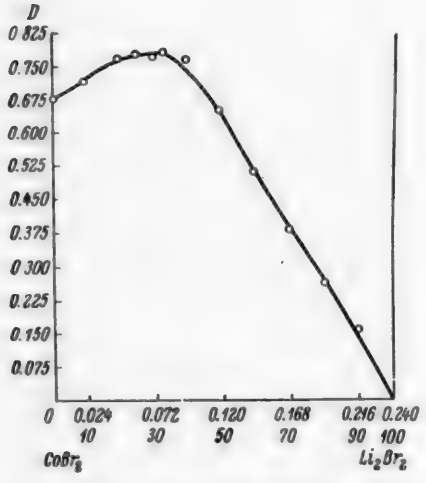

Fig. 5. Optical density (D) of the $CoBr_2$–Li_2Br_2–(H_2O)–acetone system. Total salts 0.24 mole %, thickness of layer 0.52 mm. Wavelength 685 mμ.

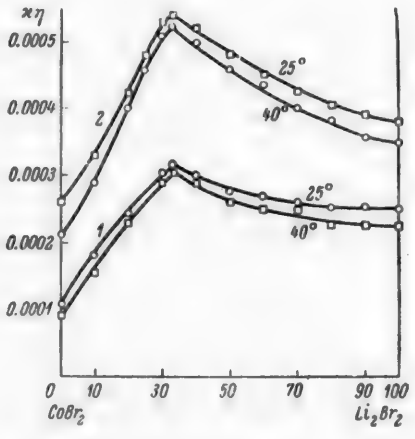

Fig. 6. Electrical conductivity, corrected for viscosity, of the $CoBr_2$–Li_2Br_2–(H_2O)–acetone system. Total salts (mole %): 1–0.12, 2–0.24.

Each of the $\kappa\eta$ – composition curves consists of two parts, intersecting in a point, whose abscissa corresponds to the ratio $CoBr_2$: Li_2Br_2 = 2:1, which indicates that the compound $CoBr_2 \cdot LiBr$ is formed in the system. The maxima of the κ – composition curve also correspond to the compound $CoBr_2 \cdot LiBr$. Studying the light absorption of the $CoBr_2$–Li_2Br_2–(H_2O)–acetone system also indicates the formation in it of the more complex cobaltobromide compound $CoBr_2 \cdot 2LiBr$. Investigation of the electrical conductivity and viscosity of this system confirms the formation of only the compound $CoBr_2 \cdot LiBr$. This discrepancy is explained by the fact that light absorption is more sensitive to the formation of complex cobaltobromide compounds in the system.

The results of the investigation given above for diagonal and the side of the system show that the formation of complex cobaltobromide compounds in the $Co(ClO_4)_2$–Li_2Br_2–(H_2O)–acetone system proceeds stepwise:

$$Co(ClO_4)_2 + Li_2Br_2 = CoBr_2 + 2LiClO_4$$

$$2CoBr_2 + Li_2Br_2 = 2(CoBr_2 \cdot LiBr)$$

$$2(CoBr_2 \cdot LiBr) + Li_2Br_2 = 2(CoBr_2 \cdot 2LiBr)$$

The study carried out on the systems above, which form part of the quaternary system, showed that interaction of the salts was observed in the side system $CoBr_2$–Li_2Br_2 and the diagonal system $Co(ClO_4)_2$–Li_2Br_2. In the other side systems and diagonal system $CoBr_2$–$(LiClO_4)_2$, we did not detect interaction between the salts. The salt pair $CoBr_2$–$(LiClO_4)_2$, forms the stable diagonal in this quaternary system and the salts $Co(ClO_4)_2$–Li_2Br_2

form the unstable diagonal.

SUMMARY

1. The $Co(ClO_4)_2$–Li_2Br_2–(H_2O)–acetone system was investigated by physical chemical analysis methods.

2. Light absorption, electrical conductivity and viscosity of the solutions were studied.

The most "sensitive" properties to the formation of cobaltobromide compounds in the system were light absorption and electrical conductivity. Light absorption is not only a sensitive, but also a selective property.

3. Interaction of the salts was detected in the diagonal system $Co(ClO_4)_2$–Li_2Br_2 and the side system $CoBr_2$–Li_2Br_2.

4. On the optical density isotherms of the $Co(ClO_4)_2$–Li_2Br_2–(H_2O)–acetone system with 0.12 and 0.24 mole % total salts, we observed the formation of the compounds $CoBr_2$, $CoBr_2 \cdot LiBr$, $CoBr_2 \cdot 2LiBr$. We observed the formation of the compound $CoBr_2 \cdot LiBr$ only on the electrical conductivity isotherms.

5. The formation of the compound $CoBr_2 \cdot LiBr$, in the system we investigated, was confirmed on the isotherms of a series of properties (optical density, electrical conductivity and $\kappa\eta$). The abscissa of the characteristic point (composition), corresponding to the formation of the compound $CoBr_2 \cdot LiBr$, in the system, remained constant in the region of stable composition with change in temperature and concentrations of the salts.

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DIPOLE MOMENTS OF COMPLEX COMPOUNDS OF STANNIC CHLORIDE WITH SOME ORGANIC ACIDS. XI.

O. A. Osipov, G. S. Samofalova and E. I. Glushko

A number of investigators have studied the complex compounds of stannic chloride with organic acids. Pfeiffer [1] showed, in 1910, that $SnCl_4$ reacts with carboxylic acids to form complex compounds $SnCl_4 \cdot 2RCOOH$, in which the coordination number of tin was equal to six. However, an investigation of the viscosity and electroconductivity [2] of the $SnCl_4$–CH_3COOH system showed that the maximum of the viscosity isotherm and minimum of the electroconductivity curve corresponded to 25 mole % of stannic chloride, i. e., the complex compound $SnCl_4 \cdot 3CH_3COOH$ was formed. M. I. Usanovich and E. I. Kalabanovskaya [3, 4], reinvestigated the viscosity and electroconductivity of the $SnCl_4$–CH_3COOH system over a wide temperature range but also did not detect the compound $SnCl_4 \cdot 2CH_3COOH$, although they were able to isolate this compound by a preparative method. Usanovich and Kalabanovskaya considered the complex $SnCl_4 \cdot 2CH_3COOH$ [3, 4] as a strongly dibasic acid. The compound $SnCl_4 \cdot 3CH_3COOH$, however, they considered as the product of the acid-base reaction of the acid $SnCl_4 \cdot 2CH_3COOH$ with the base CH_3COOH, similarly to the formation of the compound $H_2SO_4 \cdot 3CH_3COOH$. They likewise isolated the compound $SnCl_4 \cdot 3HCOOH$ [4]. T. Sumarokova and F. Yakovleva [5] used physical chemical analysis methods to investigate systematically the systems formed by $SnCl_4$ with a series of organic acids. On the basis of the data obtained, the authors concluded that the strength of complex acids of the type $SnCl_4 \cdot 2RCOOH$ decreased with an increase in the size of the oxonium base radical, and that the formation of compounds of the type $SnCl_4 \cdot 3RCOOH$ was a secondary acid-base reaction of the strong acid $SnCl_4 \cdot 2RCOOH$ with the base RCOOH.

An analogous phenomenon was observed in the formation of complex compounds of boron trichloride with acetic acid and alcohol. Besides the equimolecular compounds of BF_3 with CH_3COOH and C_2H_5OH [6], the complex compounds $BF_3 \cdot 2CH_3COOH$, $BF_3 \cdot 2H_2O$, $BF_3 \cdot 2C_2H_5OH$ etc. were obtained [7,8]. E. A. Nikitina [9] considered that two molecules of water, acid and alcohol (capable of association due to a hydrogen bond) occupy one coordination position in the complex compounds $BF_3 \cdot 2CH_3COOH$, $BF_3 \cdot 2H_2O$ and $BF_3 \cdot 2C_2H_5OH$. However, A. V. Topchiev and Ya. M. Paushkin [10], expressed a different opinion. They considered that the nature of the bond of BF_3 with the second ligand molecule was different to the first. The addition of the first ligand molecule to BF_3 was due to the formation of a new coordination bond between the acceptor, boron, and the electron donor, oxygen; the addition of a second molecule, however, may be explained by salt formation by an acid-base type of reaction.

It seemed to us that an investigation of the dipole moments of such compounds could help considerably to clarify the nature of the bonds mentioned.

In the present work, we give the results of investigating the dipole moments of complex compounds, formed by stannic chloride with two or three molecules of acetic, chloroacetic, trichloroacetic and benzoic acids.

We have previously described [11] the methods used for the determination of dielectric permeability, refractive index and density, the purification of $SnCl_4$ and benzene, as well as the preparation of solutions of complex in benzene. We shall only note here that the carefully purified acetic acid and its chloro substituted derivatives had the following boiling points: CH_3COOH 118.1° (754 mm), $CH_2ClCOOH$ 188.9° (748 mm), CCl_3COOH 196.3° (742 mm). Benzoic acid (chemically pure) after sublimation had m. p. 122.4°.

Investigation Results and Discussion

Let us first examine the data obtained for acetic acid and its chloro derivatives. Tables 1-6 give the results of measurements of dielectric permeability (ϵ), density (d) and calculated polarization values (P_2) for complex compounds of stannic chloride with two and three molecules of acetic, monochloroacetic and trichloroacetic acids in benzene in relation to the concentration of the corresponding complex. The complex compound of stannic chloride with two molecules of the $SnCl_4 \cdot 2CH_3COOH$ acid has a polarization, extrapolated to infinite dilution (P_∞), equal to 920 cm^3 and a deformation polarization ($P_D = P_E + P_A$) equal to 69.48 cm^3.

The electronic polarization (P_E) was determined from the refraction of the complex compounds and the atomic polarization (P_A) we considered equal to 15% of the molar refraction, as accepted in the literature [12]. The calculated value of the dipole moment (μ) of the complex $SnCl_4 \cdot 2CH_3COOH$ is equal to 6.38 D. For the compound $SnCl_4 \cdot 3CH_3COOH$ these values are equal to 1166, 84.93 cm^3 and 7.23 D, respectively. For the complex compound $SnCl_4 \cdot 2CH_2ClCOOH$ $P_\infty = 330$ cm^3, $P_D = 82.06$ cm^3 and the dipole moment $\mu = 3.44$ D. These values for the compound with composition $SnCl_4 \cdot 3CH_2ClCOOH$ are equal to: 378, 100.07 cm^3 and 3.67 D. For the mixture $[SnCl_4 + 2CCl_3COOH]$ $P_\infty = 195$ cm^3, P_D 104.39 cm^3 and $\mu = 2.09$ D. For the mixture $[SnCl_4 + 3CCl_3COOH]$, however, these values are equal to 220, 135.75 cm^3 and 1.89 D, respectively.

TABLE 1

The Complex $[SnCl_4 \cdot 2CH_3COOH]$ in benzene $P_\infty = 920$ cm^3, R= 60.42 cm^3, μ=6.38 D.

c in mole fractions	ϵ	d	P_2
0.0025	2.421	0.8832	894
0.0050	2.561	0.8855	873
0.0100	2.862	0.8949	847
0.0150	3.208	0.9075	830
0.0200	3.576	0.9174	818
0.0250	3.975	0.9282	803
0.0300	4.378	0.9391	800

TABLE 2

The Complex $[SnCl_4 \cdot 2CH_3COOH]CH_3COOH$ in benzene P_∞ = 1166 cm^3, R= 73.85 cm^3, μ= 7.23 D.

c in mole fractions	ϵ	d	P_2
0.0037	2.556	0.8820	1162
0.0050	2.663	0.8853	1159
0.0062	2.760	0.8877	1150
0.0075	2.888	0.8910	1151
0.0100	3.125	0.8964	1154

TABLE 3

The Complex $[SnCl_4 \cdot 2CH_2ClCOOH]$ in benzene P_∞ = 330 cm^3, R=70.65 cm^3, μ = 3.44 D.

c in mole fractions	ϵ	d	P_2
0.0050	2.345	0.8840	302
0.0100	2.410	0.9005	285
0.0150	2.448	0.9136	264
0.0200	2.504	0.9218	257
0.0250	2.577	0.9356	253

TABLE 4

The Complex $[SnCl_4 \cdot 2CH_2ClCOOH]CH_2ClCOOH$ in benzene P_∞ = 378 cm^3, R = 87.02 cm^3, μ = 3.67 D.

c in mole fractions	ϵ	d	P_2
0.0050	2.364	0.8873	355
0.0100	2.431	0.9009	340
0.0150	2.503	0.9143	330
0.0200	2.567	0.9280	317
0.0250	2.616	0.9418	300
0.0300	2.692	0.9566	298

The data in Tables 1–6 show that the dipole moments of mixtures of stannic chloride with the three given acids decrease in passing from acetic to trichloroacetic acid, and the magnitudes of the dipole moments for mixtures of $SnCl_4$ with two and three molecules of trichloroacetic acid is of the same order as the moment of the acid itself (according to our preliminary data, the dipole moment of CCl_3COOH is about 1.8–1.9 D). Such a

sharp fall in orientation polarization and dipole moment in passing from a mixture of $SnCl_4$ with acetic acid to mixtures of $SnCl_4$ with its chloro derivatives indicates a considerable decrease in the stability of the complex compounds, formed with $SnCl_4$ and chloro derivatives of acetic acid in comparison with the compounds $SnCl_4 \cdot 2CH_3COOH$ and $SnCl_4 \cdot 3CH_3COOH$.

The exchange of a hydrogen atom in acetic acid for a more electronegative chlorine atom causes an inductive displacement of electronic density towards the chlorine atom. Such a displacement of electronic density decreases the donor properties of oxygen and, as a result, the donation of an electron pair to the electron acceptor, tin, is made more difficult and this leads to a weakening of the donor-acceptor bond and, consequently, to a decrease in complex stability. The higher the electrophilicity of the electronegative group, the weaker the manifestation of donor properties of the hydroxyl oxygen and, consequently, the complex is that much less stable.

The dipole moment of complex $SnCl_4 \cdot 2CH_3COOH$ μ =6.38 D is 4 D greater than the dipole moment of acetic acid μ = 1.7 D*.

Consequently, we may consider that in the first approximation, 2 D are allotted to each Sn—O bond. The dipole moment of complex $SnCl_4 \cdot 3CH_3COOH$ is equal to 7.23 D.

Thus, the addition of a third acetic acid molecule increases the dipole moment of the complex only by 0.85 D. From this phenomenon we can assume that the nature of the bond of the third molecule differs from that of the first two acetic acid molecule bonds with $SnCl_4$.

From the data obtained, we can assume that the complex compounds $SnCl_4 \cdot 2CH_3COOH$ is formed as a result of the donor-acceptor bond between tin and the oxygen of the ester group, while the third acetic acid molecule is added to $SnCl_4 \cdot 2CH_3COOH$, as to a strong acid, due to a dipole reaction, i.e., it is located in the outer sphere. These data agree with the results of investigations by Usanovich et al.

TABLE 5

The Complex $SnCl_4$–$2CCl_3COOH$ in benzene R=89.5 cm^3 P_∞ = 195 cm^3, μ = 2.09 D

c in mole fractions	ε	d	P_2
0.0050	2.300	0.8875	196
0.0100	2.318	0.8964	195
0.0150	2.347	0.9098	194
0.0200	2.382	0.9242	200
0.0250	2.419	0.9425	199

TABLE 6

The Complex $SnCl_4$–$3CCl_3COOH$ in benzene P_∞ = 220 cm^3, R =118.05 cm^3, μ = 1.89 D.

c in mole fractions	ε	d	P_2
0.0050	2.303	0.8944	216
0.0100	2.326	0.9147	208
0.0150	2.346	0.9327	206
0.0200	2.369	0.9513	202
0.0250	2.391	0.9737	198

Thus, the complex compound of stannic chloride with three acetic acid molecules may be expressed as follows: $[SnCl_4 \cdot 2CH_3COOH]\ CH_3COOH$. The same may be said of the complex compounds $SnCl_4 \cdot 2CH_2ClCOOH$ and $SnCl_4 \cdot 3CH_2ClCOOH$. As can be seen from the data in Tables 2 and 3, in adding a chloroacetic acid molecule to $SnCl_4 \cdot 2CH_2ClCOOH$, the dipole moment increases only by 0.23 D, which shows that the thermal stability of the complex $SnCl_4 \cdot 3CH_2ClCOOH$ is small in comparison with that of $SnCl_4 \cdot 3CH_3COOH$.

If complex formation between $SnCl_4$ and trichloroacetic acid is judged by the value of the dipole moment, we must conclude that the complex compound $SnCl_4 \cdot 3CCl_3COOH$ cannot generally form. Such a conclusion agrees with the results of physical chemical analyses of $SnCl_4$–CCl_3COOH systems [5].

We noted above that the introduction of an electrophilic chlorine atom into an acetic acid molecule resulted in a sharp decrease in the dipole moment of the complex compound with stannic chloride and equally decreases its stability. From this point of view, it was interesting to investigate the decrease in the value of the dipole moment and stability of the complex when exchanging acetic for benzoic acid, in which the C_6H_5 radical is more electrophilic than the CH_3 radical.

* We assume that 2 acetic acid molecules are located at an angle of 90° to each other in the complex, then the difference will be equal to the moment of the complex minus the moment of the polar component, multiplied by $\sqrt{2}$.

Tables 7 and 8 give the results of measurements of dielectric permeability, density and calculated polarization values for complex compounds of stannic chloride with two and three benzoic acid molecules in benzene in relation to complex concentration. For the complex compound $SnCl_4 \cdot 2C_6H_5COOH$ $P_\infty = 780$ cm^3, $P_D =$ 103.62 cm^3 and $\mu = 5.73$ D. However, for the complex compound $SnCl_4 \cdot 3C_6H_5COOH$ $P_\infty = 900$ cm^3, $P_D =$ 133.86 cm^3 and $\mu = 6.10$ D. As seen from this data, here, as in the acetic acid case, the addition of the first two benzoic acid molecules to $SnCl_4$ results in a sharp increase in the dipole moment in comparison with the moment of C_6H_5COOH. The addition of the third molecule, however, increases the moment only by 0.37 D. The data given again confirm that the first two acid molecules are bonded to $SnCl_4$ by coordination, while the addition of the third molecule occurs as a result of an electrostatic reaction of the $SnCl_4 \cdot 2C_6H_5COOH$ complex with a molecule of C_6H_5COOH.

TABLE 7

The Complex [$SnCl_4 \cdot 2C_6H_5COOH$] in benzene R = 89.70 cm^3, $P_\infty = 780$ cm^3, $\mu = 5.73$ D

c in mole fractions	ε	d	P_2
0.005	2.538	0.8907	815
0.0075	2.710	0.8970	854
0.0100	2.869	0.9025	868
0.0125	3.044	0.9089	870
0.0150	3.264	0.9145	897
0.0200	3.706	0.9276	908

TABLE 8

The Complex [$SnCl_4 \cdot 2C_6H_5COOH$] C_6H_5COOH in benzene R = 116.25 cm^3, $P_\infty = 900$ cm^3, $\mu =$ 6.16 D

c in mole fractions	ε	d	P_2
0.005	2.578	0.8920	960
0.0075	2.744	0.8989	1000
0.0100	2.964	0.9059	1010
0.0125	3.222	0.9134	1060
0.0150	3.493	0.9207	1088

In comparing the value of the dipole moment of $SnCl_4 \cdot 2CH_3COOH$ ($\mu = 6.38$ D) with that of $SnCl_4 \cdot 2C_6H_5$ COOH ($\mu = 5.75$ D) or $SnCl_4 \cdot 3CH_3COOH$ ($\mu = 7.23$ D) with that of $SnCl_4 \cdot 3C_6H_5COOH$ ($\mu = 6.1$ D), we see that the substitution of the CH_3 for the C_6H_5 radical in the acid results in a decrease in the dipole moment of the complex and, consequently, in its degree of stability. According to our preliminary data, the heat of formation of $SnCl_4 \cdot 3C_6H_5COOH$ is less than the heat of formation of $SnCl_4 \cdot 3CH_3COOH$, which agrees with the results of dipole moment investigations.

SUMMARY

1. The dipole moments of the complex compounds $SnCl_4 \cdot 2CH_3COOH$ and $SnCl_4 \cdot 3CH_3COOH$, $SnCl_4 \cdot 2CH_2ClCOOH$ and $SnCl_4 \cdot 3CH_2ClCOOH$, $SnCl_4 \cdot 2C_6H_5COOH$ and $SnCl_4 \cdot 3C_6H_5COOH$, were determined, as well as of mixtures of $SnCl_4$ and trichloroacetic acid.

2. It was shown that the reaction of stannic chloride with the first two molecules led to a sharp increase in the dipole moment, while the addition of the third molecule only produced a small change in the value of the moment. We concluded from this that only the first two acid molecules are bonded to $SnCl_4$ by coordination and that the third molecule is located in the outer sphere and has a different type of bond.

3. It was shown that with an increase in the electrophilicity of the acid radical, the value of the dipole moment and degree of stability of the complex decrease.

4. On the basis of dipole moment determinations, it was shown that the complex compound $SnCl_4 \cdot 3CCl_3$ COOH does not form.

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THE PROBLEM OF DETECTING CADMIUM WITH p-NITROPHENYLDIAZOAMINO-AZOBENZENE (CADION)

V. P. Razumova

Dwyer [1] discovered a very sensitive and specific reagent for cadmium, p-nitrophenyldiazoaminoazobenzene $NO_2C_6H_4O{=}NNHC_6H_4N{=}NC_6H_5$, which he named "cadion.". Later, the same author proposed as cadmium reagents two more azo dyes, that were more sensitive but less stable.

However strange it may seem, there is not one opinion expressed in the literature on the composition or the properties of cadion. Dwyer assumes that the presence of an azo group is necessary for a reaction with cadmium; Kulberg does not consider it necessary [2]; in a well-known handbook [3] the reagent is called p-nitrophenyldiazoamino-p-azobenzene while on the next page, where its synthesis is described, it is called p-nitrophenyldiazoamino-p-benzene.

Different melting points are also given: 197°[1], 186.5°[4], 151°[3]. There is no mention anywhere of the stability of cadion solutions. Finally, more convincing proof of the adsorptive character of the cadmium reaction with cadion would be appreciated.

Synthesis of Cadion

The cadion was synthesized exactly as described by Dwyer.

According to Dwyer's directions, this method leads to a crystalline product in the form of yellow needles, with m. p. 197°. We obtained, however, an amorphous yellow precipitate with m. p. 142° that could not be dried. Because of this, we purified it in the way usually used for such cases– boiling an alkaline alcohol solution (2 drops of strong ammonia solution per 600 ml of ethyl alcohol) several times with animal charcoal. As a result, we obtained fine orange needles; when heated to 192° the cadion darkened and at 197° it melted, but if heated further it decomposed with a slight explosion.

Cadion is insoluble in water, dissolves slightly in ethyl alcohol, and more readily, in benzene and acetone it dissolves readily in ether and ethyl alcohol containing a few drops of ammonia, potassium hydroxide or sodium hydroxide, to give a crimson, almost violet solution. Cadion is rapidly decomposed by mineral acids; dilute acetic acid has no effect on it.

The reagent for cadmium detection was prepared according to Dwyer's directions, by dissolving 0.02 g of cadion in 100 ml of ethyl alcohol containing 1 ml of 2 N KOH. To check the stability of this solution, we took two portions and passed a fast current of carbon dioxide through one and oxygen through the other for 15 minutes. Under CO_2 treatment the solution rapidly became yellow and a yellow precipitate was formed. The precipitate dissolved on adding a few drops of 2 N KOH and the solution again became violet. The passage of oxygen under the same conditions did not noticeably affect the solution.

As carbon dioxide is always present in air, we do not recommend preparing a cadion solution for storage and, in any case, it should be kept in a well-sealed bottle.

Some Chemical Properties of Cadion

An alkaline alcohol solution of cadion is of a crimson, almost violet color; reaction with cadmium gives an orange compound and with magnesium– a blue one.

We used chromatographic analysis to establish the chemical nature of cadion. Aluminum oxide, prepared by a method* proposed by E. N. Gapon and G. M. Shuvaeva [5] was used as adsorbent. With this aluminum oxide we obtained a chromatogram of an alkaline alcohol cadion solution which had three bands (Fig. 1, 1): at the top – a rather wide, violet band, then – an orange ring and below that – a wide, pale yellow band.

Several 5–7 ml portions of solvent (ethyl alcohol with a few drops of 2 N KOH) were passed through the column and it was eluted (pumping out). As a result we obtained three eluates– yellow, orange and violet. The addition of several drops of 2 N KOH made the yellow and orange eluates also violet in color. All three eluates were used for the usual qualitative reaction for Cd^{++}; it was positive in all cases. Then all three eluates were again passed through a chromatographic column with Al_2O_3, which gave chromatograms similar to the first, i. e., there was again a separation into three bands – violet, orange and yellow. From this, we assumed that the existence of different forms of cadion was due to different pH values.

To check this hypothesis we prepared a chromatogram of an alcohol solution of a universal indicator,** also on Al_2O_3. It separated into two bands– green and yellow (Fig. 1, 3). Similarly, we prepared a second chromatogram of the universal indicator in alcohol containing several drops of 2 N KOH. It separated into four bands– violet, blue, green and yellow (Fig. 1, 4). Thus, the pH changed along the whole of the adsorption column, decreasing from top to bottom, due to the gradual adsorption of alkali which occurred to a greater degree at the top of the column and less at the bottom. Consequently, the cause of the separation of the cadion into three different forms was the changes in pH.

After this, we prepared a chromatographic column from a mixture of Al_2O_3 and $Cd(OH)_2$.*** An alkaline alcohol cadion solution was passed through it also. Figure 1, 2 shows that the chromatogram separated into blue, with a weak violet tinge, red-orange, orange and yellow bands.

* 100 g of pure aluminum turnings (99.99% aluminum) was dissolved in 1 liter of a 30% NaOH solution and diluted with distilled water to 2% concentration, calculated for Al_2O_3. CO_2 was passed into the solution at 70-80° till all the $Al(OH)_3$ had precipitated. The precipitate was filtered off and washed with hot water until pH 8.0 (phenolphthalein). The aluminum hydroxide obtained was dried at 100-180°, ground in a porcelain mortar and fired for ten minutes in an electric muffle furnace at 800°.

An aqueous suspension of the aluminum oxide was introduced into a chromatographic column and pumped out.

** An indicator with a range of pH from 3 to 11. Its composition was: 0.04 g of methyl orange, 0.02 g of methyl red, 0.12 g of o-napthol phthalein and 0.08 g of phenolphthalein per 100 ml of 70% alcohol.

On increasing the pH of the solution the indicator became successively red, orange, yellow, green, blue and violet in color.

***For this, dry aluminum oxide prepared by the method given above, was thoroughly mixed in a porcelain mortar with dry cadmium hydroxide in a 1 : 1 ratio, the mixture was placed in a column and packed down by knocking against a hard surface till there was no more settling. (The experiments were carried out with both dry and wet columns. In practice, wet columns did not have any advantages over dry ones).

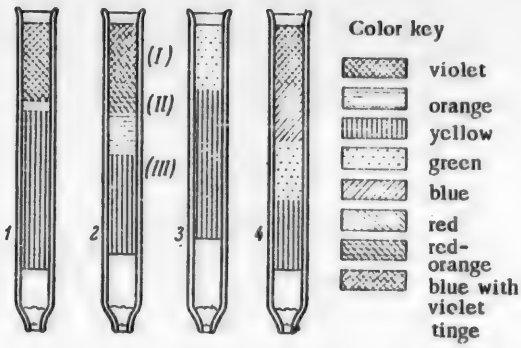

Fig. 1. Chromatograms, obtained on adsorbing solutions. 1) Alkaline alcohol cadion solution on Al_2O_3, 2) alkaline alcohol cadion solution on a mixture of Al_2O_3 and $Cd(OH)_2$, 3) alcohol solution of universal indicator on Al_2O_3, without alkali, 4) alcohol solution of universal indicator on Al_2O_3 with the addition of 2 N KOH. Explanation in the text.

The column was cut into three parts and the blue (I), red-orange and orange (II) and yellow (III) parts of the column were extracted with ether (cadion dissolves readily in ethyl ether). All the extracts acquired a yellow shade, apparently, because the alkali was not extracted by the ether, the pH decreased and these forms all became one yellow form, that exists at a low pH value. The adsorbent, remaining from extraction of (I) and (II), became red (Fig. 2), and that from (III) remained yellow.

Thus, the orange form is the adsorption compound of $Cd(OH)_2$, with the red and yellow forms of cadion. The compound with the yellow form is less stable than that with the red form, as a result of which the yellow form is first extracted with ether while the red one remains, and is extracted later only after several ether extractions.

Similar chromatograms were obtained on filter paper by carrying out the reaction for Cd^{++} with one drop (Fig. 3, 2) and by treating filter paper with alkaline alcohol cadion solution alone (Fig. 3, 1). The difference between these two colored spots was that in the presence of cadmium there was an orange spot in the middle, then blue with a pale violet shade around and a yellow border; in the presence of the alkaline alcohol cadion solution alone, there was no orange spot, in the middle it was crimson-violet, with a yellow border. This occurred as a result of Cd^{++} combining with the red and yellow variations of the three forms, giving rise to an orange spot in the center, with a blue ring around the edge.

These investigations indicate that three forms of cadion exist– blue, red and yellow, which interconvert at various pH values. The red and yellow forms react with Cd^{++} and as a result form the orange compound.

To confirm this conclusion, we investigated an alkaline alcohol solution of cadion at various pH values.

Investigation of the Properties of an Alkaline Alcohol Solution of Cadion at Various pH Values.

For the investigation, we used an alkaline alcohol cadion solution which was 0.02% with respect to cadion and 0.02 N with KOH. The extinction (E) of this solution was measured on a FEK-2 in the wavelength range

* The color designations are for all the figures.

500–600 mμ at various pH values. The pH was changed by adding 0.02 N CH_3COOH solution. The pH was regulated with a glass electrode. When a precipitate formed the cadion solution was rapidly filtered off by pumping through a dry, No. 4, glass filter into a dry flask. The data obtained are given in the table and in Fig. 4.

From the data given it can be seen that cadion is similar to an indicator with three transition ranges:

(I) pH < 11.00 (yellow solution),
(II) from pH 11.00 to pH 11.65 (orange-red solution),
(III) pH > 11.65 (violet solution)

One can conclude from this, that the red and blue forms of cadion exist at similar pH values, which makes solutions with pH > 11.65; violet in color; they may be separated in a chromatographic column on mixtures of Al_2O_3 and $Cd(OH)_2$ (Fig. 1, 2); the blue form may also be separated from the red and yellow forms on filter paper, as occurred in the spot reaction for Cd^{++} with cadion (Fig. 3, 2). The yellow form exists over the whole range of pH values investigated and, together with the red form, it gives an orange-red color to solutions with pH from 11.00 to 11.65.

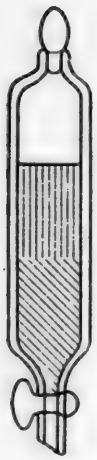

Fig. 2. Preparation of ether extracts from parts (I) and (II) of the adsorption column, drawn in Fig. 1, 2 (the adsorbent became red in color, and the extract yellow).

The nature of the reaction between cadmium and cadion

We also used chromatographic analysis for determining the character of the reaction between cadmium and cadion. For this purpose we used the chromatographic column drawn in Fig. 1, 2, where an alkaline alcohol cadion solution was adsorbed on a mixture of Al_2O_3 and $Cd(OH)_2$. As mentioned above, the column was cut into three parts and the red-orange and orange sections of the tube were investigated.

pH	Extinction of the solution (*E*)	Remarks
13.00	1.60	Violet solutions. At pH 11.70 a yellow precipitate of cadion started to form
12.85	1.55	
12.00	1.50	
12.00	1.50	
11.80	1.45	
11.80	1.50	
11.70	1.30	
11.70	1.35	
11.65	1.20	Red solutions with yellow precipitate
11.65	1.25	
11.55	0.90	
11.55	0.70	
11.45	0.17	
11.00	0.10	Yellow solutions with yellow precipitate
11.00	0.09	
10.00	0.09	
10.00	0.09	
8.60	0.08	
8.00	0.07	
7.55	0.06	
6.55	0.04	
6.00	0.03	
2.65	0.02	

The colored adsorbent [Al_2O_3 and $Cd(OH)_2$] was transferred to a separating funnel, where it was shaken for a long time with separate portions of ethyl ether. At first the adsorbent became red and then paler and paler. The ether extract was yellow. The extraction was continued until the adsorbent became almost colorless.

The ether extract was evaporated, the organic materials oxidized with conc. HNO_3, H_2SO_4 added to the solution and after removal of the oxidant by boiling and evaporating to SO_3 vapor, a reaction for Cd^{++} was carried

out in the solution by two methods – microcrystalloscopic (reaction with $(NH_4)_2[Hg(CNS)_4]$), and cadion, by Dwyer's method. In both cases the reaction was negative, the Cd^{++} was not detected, it remained in the precipitate.

This result confirmed the opinions of Dwyer, Adamovich and Novik on the adsorptive character of the reaction between cadion and Cd^{++}.

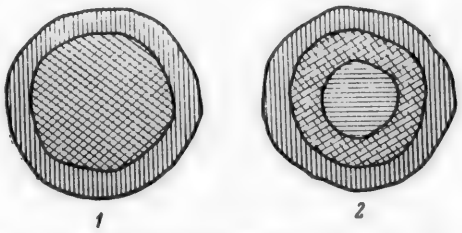

Fig. 3. Chromatogram obtained on filter paper. 1) Treated with an alkaline alcohol cadion solution; 2) treatment of a drop of solution containing Cd^{++} with an alkaline alcohol solution of cadion and 2 N KOH.

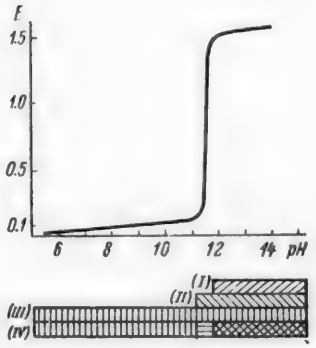

Fig. 4. Determination of the transition ranges of cadion at various pH values. (I) - blue form, (II) - red form. (III) - yellow form, (IV) - color obtained by superimposing the three colors– yellow with red (red-orange) and blue with red (violet).

SUMMARY

1. Cadion (p-nitrophenyldiazoaminoazobenzene) is similar to an indicator with three transition ranges.

2. One can assume the existence of three forms in an alkaline alcohol cadion solution – yellow, red and blue. The red and blue exist at values of pH> 11.65, making the solution violet. The yellow form exists over all the pH range investigated (from 5 to 13).

3. It was confirmed that the reaction between Cd^{++} and cadion is adsorptive in character.

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THE POLAROGRAPHIC BEHAVIOR OF GEOMETRICALLY ISOMERIC ACIDS

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According to Auwers and Wissebach's data [1], of two geometric isomers the trans-isomer, as a rule, is distinguished by a lower density and a smaller refractive index than the cis-isomer; however, the esters of tiglic and angelic acids show the opposite relationships. According to Langseth [2], trans-forms always have a higher melting point than the cis-forms. Stoermer and Heymann [3], stated that the trans-isomers of α-chloro-, β-chloro-, α-bromo- and dibromocinnamic acids melt at higher temperatures and are less soluble in water than the cis-forms and, at the same time, they noted that, on the contrary, the cis-forms of β-bromo-cinnamic and dichlorocinnamic acids are less soluble in water and have higher melting points than the trans-forms. In the same way, the melting point does not indicate either a cis- or a trans-configuration for the esters of halogen substituted cinnamic acids, as many of the trans-forms are compounds with lower melting points than those of the corresponding cis-forms [4].

Attempts were made to use spectographic data for determining the structure of crotonic acids. However, Auwers [5] considered that the configuration of stereoisomers could not be determined accurately from spectrographic investigations.

We decided to use the indices of the polarographic behavior of geometric isomers in investigating their structure, considering that the difference in the free energy of reduction of isomers must affect their capacity for reduction at an electrode. In passing, we determined the conditions for the quantitative analysis of mixtures of cis- and trans-isomers, which are, generally speaking, isolated with difficulty and, therefore, are difficult to analyze quantitatively by all the methods which require a separation of the mixture's components.

We used geometrically isomeric carboxylic acids of the ethylene series for our investigations. Of these, only maleic and fumaric acids had previously been subjected to a thorough polarographic investigation [6–13]. All the authors noted that maleic acid was reduced at a lower (in absolute value) potential than fumaric acid and in different media the difference in reduction potentials varied from 0.05 to 0.5 v.

Citraconic and Mesaconic acids

Citraconic acid was synthesized by Shriner, Ford and Roll's method [14]. Mesaconic was prepared from citraconic acid by boiling the latter with dilute nitric acid and subsequently evaporating the solution till the appearance of red vapor [15]. After recrystallization from water, the acid had m. p. 201°.

We used potassium chloride, disodium hydrogen phosphate, citric acid, boric acid, sodium hydroxide and hydrochloric acid of analytical purity as indifferent electrolytes. The dry salts were first recrystallized. The mercury for the dropping electrode was purified by the method described by Mislovitser [16]. McIlvain's buffer mixtures on 1 N potassium chloride solution were used to establish the effect of pH on the polarographic behavior of the acids.

The polarographic investigations were carried out with a visual polarograph M-7-2000. A saturated calomel electrode was used as the anode (all potential values are given in relation to this anode). The capillary characteristic (at m=1.12 mg/sec. and t=5 sec.) $m^{2/3} \cdot t^{1/6} = 1.41\ mg^{2/3} \cdot sec^{1/2}$. The galvanometer sensitivity was 1.37×10^{-8} A/mm. All determinations were carried out in a thermostat at 25 ± 0.2°.

Both the citraconic and mesaconic acids gave clear polarographic waves in the pH interval from 0.02 to 3.38. As backgrounds with pH from 3.38 to 6.62 each acid gave two waves; as the pH increased the first wave

(at the more positive potential) decreased in height and finally disappeared; the second wave (at the more negative potential) increased in height and at pH > 6.62 only the second wave remained. Neither the citraconic or mesaconic acids were reduced at a dropping mercury cathode at pH = 9 and above.

As the pH of the medium increased, the half-wave potentials of both acids were displaced towards more negative values (Table 1). In all the range of pH values investigated, the half-wave potentials of both acids were found to be very close, so that when the two were present in the solution, the waves of both acids combined into one wave.

The coefficient of proportionality between the diffusion current and acid concentration in solutions of 0.1 N HCl was 4.46 μA/mmole/liter for citraconic and 6.40 μA/mmole/liter for the mesaconic acid.

The effect of substituting aqueous alcohol and alcohol media for the aqueous one is clearly seen from the data in Table 2. A 1 N hydrochloric acid solution was used as background for this series of experiments.

TABLE 1

pH	Citraconic acid				Mesaconic acid			
	1st wave		2nd wave		1st wave		2nd wave	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0.02	—0.61	36.99	—	—	—0.68	41.11	—	—
1.14	—0.68	45.21	—	—	—0.72	57.54	—	—
2.55	—0.80	46.63	—	—	—0.88	54.80	—	—
3.38	—0.81	24.66	—1.01	21.92	—0.92	21.92	—1.15	28.77
5.42	—0.92	19.18	—1.17	28.77	—0.98	15.33	—1.22	23.29
6.62	—1.17	9.59	—1.42	31.51	—1.21	5.48	—1.45	11.64
7.50	—	—	—1.51	39.77	—	—	—1.45	3.08
8.00	—	—	—1.51	32.88	—	—	—1.45	3.56

TABLE 2

Alcohol concentration (in %)	Citraconic acid		Mesaconic acid	
	$E_{1/2}$	i_d (μA)	$E_{1/2}$	i_d (μA)
0	—0.62	37.88	—0.69	44.69
25	—0.68	22.26	—0.79	25.62
50	—0.72	26.28	—0.86	19.86
75	—0.75	24.25	—0.96	20.13
100	—0.77	23.29	—	—

The concentrations of the acids investigated were equal to $1 \cdot 10^{-3}$ M in all the experiments.

Polarographic investigations of citraconic and mesaconic acids in various media showed that citraconic acid was polarographed as well in aqueous as in aqueous alcohol and alcohol media, while mesaconic acid was readily polarographed in water, but was not polarographed at all in anhydrous alcohol.

The relation between diffusion current and concentration was determined for all aqueous alcohol backgrounds with 1 N hydrochloric acid (Table 3). In all cases direct proportionality was observed between the magnitude of the diffusion current and acid concentration.

TABLE 3

Medium	$\frac{i_d}{C}$ for acids $\left(\frac{\mu A}{mmole \cdot liter}\right)$	
	citraconic	mesaconic
Water	3.790	4.430
25% alcohol	2.386	2.491
50% alcohol	2.618	1.985
75% alcohol	2.469	2.116
100% alcohol	3.057	—

The data in Table 2 show that the half-wave potentials of both acids, in 1 N hydrochloric acid in 75% aqueous alcohol solution, differ by 0.2 v, which makes it possible to determine citraconic and mesaconic acids polarographically when they are present together. Under these circumstances, two definite waves were obtained, one of which (at the more positive potential value) was the citraconic acid wave and the other (with the more negative potential) was the mesaconic acid wave. The half-wave potentials did not depend on acid concentration.

In checking the method with standard preparations, quite satisfactory results were obtained: the errors in determination lay within the limits of ± 2.4% of the true amount of each acid in the mixture.

TABLE 4

pH	Cis-aconitic acid				Trans-aconitic acid			
	1st wave		2nd wave		1st wave		2nd wave	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0.02	—0.54	30.14	—	—	—0.59	32.88	—	—
1.14	—0.65	30.82	—	—	—0.68	35.62	—	—
2.35	—0.74	32.56	—	—	—0.78	36.30	—	—
3.45	—0.85	39.93	—	—	—0.90	40.41	—	—
5.44	—1.02	16.44	—1.32	15.07	—1.03	18.49	—1.40	15.75
6.31	—1.05	10.27	—1.35	12.53	—1.15	2.74	—1.45	11.64
7.70	—1.25	6.16	—1.54	8.22	—1.27	1.03	—1.73	10.96
8.50	—1.33	4.79	—1.66	7.53				

TABLE 5

Alcohol concentration (in %)	Cis-aconitic acid		Trans-aconitic acid	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0	—0.54	30.14	—0.59	32.88
25	—0.61	23.29	—0.77	25.34
50	—0.63	10.96	—0.82	17.81
75	—0.67	9.97	—0.88	15.09
	—0.59	10.96	—0.81	15.07

Cis- and Trans-Aconitic Acids

Trans-aconitic acid was prepared from citric acid by V. Bruce's method [14]. Its colorless crystals had m. p. 180°. Aconitic acid anhydride was prepared from the trans-aconitic acid by Anschutz and Bertram's method [17], and the cis-aconitic acid was prepared from the anhydride by Malakhovsky and Maslovsky's method [18]. Fine, needle-like crystals were obtained with m. p. 122°.

Both geometrically isomeric acids gave definite polarographic waves in the range of pH values from 0.02 to 5.44; at pH from 5.44 to 8.5 each of the acids gave two waves; as the pH increased the first wave (more positive) decreased in height; the second also decreased as regards absolute height, although it remained greater than the first. As the pH of the medium increased the half-wave potentials of both acids were displaced towards

more negative values (Table 4). Over all the range of pH values investigated, the values of the half-wave potentials were found to be very close, with the cis-isomer being reduced at a somewhat more positive potential than the trans-isomer. When both isomers were present in the solution, their waves combined into one overall wave.

TABLE 6

pH	Cis-cinnamic acid		Trans-cinnamic acid	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0.02	Not polarographed		—1.21	4.66
1.14	Not polarographed		—1.29	5.82
2.00	—0.80	0.19	—1.37	6.03
3.00	—0.96	0.22	—1.38	6.03
4.00	—1.18	0.44	—1.41	6.99
5.00	—1.50	1.44	—1.56	4.93
6.05	—1.56	1.03	—1.59	4.66
6.90	—1.61	0.62	—1.66	3.70
8.20	—1.67	0.19	—1.67	1.37

TABLE 7

Alcohol concentration (in %)	Cis-cinnamic acid		Trans-cinnamic acid	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0	—1.42	1.44	—1.40	2.88
25	—1.42	0.96	—1.40	1.58
50	—1.51	0.79	—1.56	1.85
75	Not polarographed		—1.55	2.06
100	"	"	—1.60	3.49

TABLE 8

Alcohol concentration (in %)	Isocrotonic acid		Crotonic acid	
	$E_{1/2}$ (V)	i_d (μA)	$E_{1/2}$ (V)	i_d (μA)
0	—1.57	2.329	—1.60	2.466
25	—1.43	2.329	—1.45	1.781
50	—1.40	0.822	—1.45	1.370
75	—1.39	0.959	—1.45	1.165
100	—1.42	0.411	Not polarographed	

Cis-aconitic acid was not reduced at a dropping mercury cathode at pH 9 and above, while trans-aconitic acid stopped being polarographed at pH 8.5.

Table 5 gives the values of half-wave potentials of both isomers in relation to the alcohol content in a background, 1 N with hydrochloric acid. The separate determination of cis- and trans-aconitic acids was possible when both were present in 50% alcohol, as their $E_{1/2}$ differed by 0.2 v. In solutions with higher alcohol concentrations, the proportionality between diffusion current and acid concentration was upset, making their quantitative determination difficult.

Our experiments showed that in 1 N hydrochloric acid in 50% alcohol with both cis- and trans-aconitic acids present, two waves were actually produced, the first belonging to cis-aconitic and the second to trans-aconitic acid. The half-wave potentials did not depend on acid concentration.

The diffusion currents were proportional to the concentrations of these acids in the mixture. The proportionality coefficient was equal to 1.067 ± 0.025 μA/mmole/liter for the cis-acid and 1.749 ± 0.058 μA/mmole/liter for the trans-acid.

We checked the polarographic method of determining cis- and trans-aconitic acids when both were present in solution, with artificially made up mixtures of definite composition. The error in determination lay within the limits of ± 2.6%.

Cis- and Trans-Cinnamic Acids

Normal cinnamic acid, which is a trans-isomer, was polarographed by Semerano and Cisini [19] in a 0.1 N solution of NH_4Cl in 50% alcohol. The reduction potential was found to be 1.46 v. The latest and quite thorough work devoted to the polarographic behavior of cinnamic acid is that of Ono Shikata and Hayasi Tadao [20]. They polarographed cinnamic acid in 50% aqueous dioxane solutions at various pHs in the presence of alkali and alkaline earth metal chlorides. In neutral solutions cinnamic acid gave two waves with $E_{1/2} = -1.5$ and -2.0 v. The height of the first wave decreased when alkali was added. One wave was observed in a 0.1 N solution of lithium chloride and the authors considered that it corresponded to the reduction of the cinnamic acid anion. Cinnamic acid was not reduced in 0.1 N HCl but in 0.01 and 0.001 N HCl it again gave two waves, the first, according to the authors, corresponding to the reduction of the cinnamic acid anion, increased greatly with increase in HCl concentration while, at the same time, the second wave, corresponding to the reduction of the C=C bond, decreased. We consider that such an explanation of the behavior of cinnamic acid is improbable: the degree of dissociation of weak cinnamic acid ($K=3.6 \cdot 10^{-5}$) must fall rapidly with an increase in HCl concentration, and the wave, corresponding to anion reduction, must decrease rather than increase.

We found no data in the literature on the polarographic behavior of cis-cinnamic acid.

We used trans-cinnamic acid of analytical purity with m. p. 132°. Cis-cinnamic acid was prepared from the trans-cinnamic. For this purpose, it was brominated, then the HBr was carefully split off giving, as a result, phenylpropiolic acid with m. p. 137°. By hydrogenating the phenylpropiolic acid on a palladium catalyst, we obtained cis-cinnamic acid. For purification it was converted into the aniline salt which was recrystallized from acetone and decomposed with hydrochloric acid. It had m. p. 68° [21].

The investigation of the polarographic behavior of both geometric isomers of cinnamic acid in aqueous buffer solutions in a range of pH values from 0.02 to 9 gave the following results: cis-cinnamic acid was not reduced at a dropping mercury cathode at a pH less than 1.14; neither the cis- nor the trans-cinnamic acids gave polarographic waves at pH = 9 or higher; both acids were reduced at other pH values; the cis-form was reduced at much more positive values of half-wave potentials in acidic media up to pH 4 than the trans-form; the half-wave potentials of both acids became very close at pH = 5 and higher (Table 6). As the pH of the medium increased, the half-wave potentials of both acids were displaced towards more negative values.

With equal concentrations in the solutions ($1 \cdot 10^{-3}$ m), trans-cinnamic acid gave much higher waves than cis-cinnamic acid over all the range of pH values that were checked. Due to this, even in the pH range of 2 to 4 in which the half-wave potentials of the two isomers differed by 0.23 −0.57 v, and would have, it seemed, made it possible to determine them quantitatively together, this was, however, actually impossible due to the small values of the diffusion current for cis-cinnamic acid.

The effect of substituting aqueous alcohol and alcohol media for the aqueous medium on the polarographic behavior of cinnamic acids was investigated in 0.1 N solutions of NH_4Cl, as the cis-cinnamic acid was not reduced in hydrochloric acid media. The data obtained for $1 \cdot 10^{-3}$ M solutions are given in Table 7. With an increase in alcohol content, the half-wave potentials of both isomers were displaced towards negative values. The diffusion current for cis-cinnamic acid decreased evenly with increase in alcohol content so that at an alcohol % of 75–100 it did not give any diffusion waves. Proportionality between diffusion current and concentration was observed only in those solutions where the alcohol concentration in the background was not less than 50%. We established with special experiments that even with both isomers present together in a solution, the proportionality between diffusion current and concentration was maintained by each of them.

A determination of the concentration of both isomers in mixtures was carried out in the following way. The trans-isomer concentration was determined by taking polarograms in 0.1 N NH_4Cl and 100% alcohol. Under these conditions, we found that the proportionality coefficient was equal to 3.51 ± 0.07 μA/mmole/liter.

Then a polarogram was taken in 0.1 N NH_4Cl in 50% alcohol. An overall wave was thus obtained for both isomers. Under these conditions, $\frac{i_d}{C} = 1.849 \pm 0.055$ for trans-cinnamic and $\frac{i_d}{C} = 0.808 \pm 0.018$ for cis-cinnamic acid. The conversion coefficient from one background to another was equal to 1.849: 3.51 = 0.526, for trans-cinnamic acid.

Multiplying the value i_d, found for a solution in 100% alcohol, by 0.562 and subtracting the product from the value of i_d, found for a solution in 50% alcohol, we obtained the i_d for the cis-isomer, by which we determined its concentration in the solution.

The range of concentrations determined lie within the limits of $1 \cdot 10^{-2}$ to $5 \cdot 10^{-4}$ M.

The above method was checked with a series of artificially prepared mixtures of definite composition. The error in determination lies within the limits of ± 2.0%.

Cis- and Tarns-Crotonic Acids

Crotonic acid was synthesized from malonic acid by Auwer's method [5]. Its m. p. was 71°. From it we prepared the dibromide [22] and from the latter – tetrolic acid [23]. By hydrogenating the tetrolic acid on a palladium catalyst in an alcohol medium [20], we obtained liquid isocrotonic acid with a solidification temperature of 15°.

Crotonic acid is considered to have a trans-configuration and the isocrotonic– a cis-configuration.

Neither the crotonic or isocrotonic acids were reduced at a dropping mercury cathode in the range of pH values from 0 to 10 (in citrate-phosphate and borate buffer solutions). Both crotonic acids gave clear polarographic waves in 0.1 N NH_4Cl in water, 25, 50 and 75% aqueous alcohol solutions. Only the isocrotonic acid was reduced in 100% alcohol and 0.1 N NH_4Cl. The data obtained for solutions with $1 \cdot 10^{-3}$ M concentration are given in Table 8. In all solutions the proportionality between diffusion current and acid concentrations was maintained.

To determine quantitatively the content of both isomeric acids in mixtures, a polarogram was taken in 100% alcohol and the isocrotonic acid concentration was determined by the height of the wave (the proportionality coefficient was equal to 0.418). Then a second polarogram was taken in an aqueous 0.1 N NH_4Cl solution and the height of the wave of the overall diffusion current was determined. Knowing i_d for isocrotonic acid, we multiplied this value by the ratio of the proportionality coefficients in water and in 100% alcohol, i. e., by 5.574, and by subtracting the value obtained from the height of the overall wave, we obtained a remainder which corresponded to the diffusion current of crotonic acid; from this, knowing the proportionality coefficient $\frac{i_d}{C} = 2.535$, we could calculate the concentration of crotonic acid in the solution. The concentrations determined lay within the range $1 \cdot 10^{-2}$ to $5 \cdot 10^{-4}$ M.

The method was checked with artificially made up mixtures. The errors in determination lay within the limits of ± 4.7%.

Discussion of Results

Certain definite rules were found in the behavior of the four pairs of geometrically isomeric acids investigated by us when reduced at a dropping mercury cathode.

1. Cis-isomers were always reduced at a more positive potential, i. e., more readily than trans-isomers. This was to be expected as cis-isomers are less stable and have a greater reserve of free energy which finds expression in higher molar values of heats of combustion and in smaller heats of formation than those of trans-isomers.

This rule in polarographic analysis was observed by many authors before us, using maleic and fumaric acids as examples [6, 10-13, 24].

2. It was established for all acids investigated (except for the crotonic acids which were not reduced in the buffer backgrounds we used) that with an increase in the alkalinity of the medium the half-wave potential was displaced towards more negative values. This relation is expressed by a straight line with a 0.06–0.08 v change in $E_{1/2}$ per unit of pH (except for cis-cinnamic acid), which approximately corresponds to a reduction process, proceeding by the addition of two electrons.

We calculated the theoretical values of $E_{1/2}$ by the equation $E_{1/2} = E_0 - 0.0591$ pH, where E_0 is the half-wave potential in the reduction of the given acid at pH = 0 (in 1 N hydrochloric acid). $E_{1/2} = -0.61$ v for citraconic acid, −0.68 v for mesaconic, −0.54 v for cis-aconitic, −0.59 v for trans-aconitic and −1.21 v for trans-cinnamic acid (cis-cinnamic acid was not reduced in 1 N hydrochloric acid).

We found that the calculated values for $E_{1/2}$ agreed quite well with those found experimentally for citraconic and mesaconic acids (Table 9) at pH < 6; the calculated half-wave potentials for both isomeric aconitic acids were quite close to the experimental ones only at pH < 3. With further increase in the pH of the background, theoretically calculated $E_{1/2}$ differed increasingly from those found practically, apparently due to the fact that in neutral and especially in alkaline media, the equilibrium

$$\text{acid} \rightleftarrows \text{anion}' \rightleftarrows \text{anion}''$$

is displaced considerably to the right and the concentration of undissociated acid becomes less and less.

The formation of two waves by citraconic and mesaconic acids in the range of pH values from 3.38 to 6.62 and by cis- and trans-aconitic acids from 5.44 to 8.50 may be explained by the dissociation of the acid with simultaneous reduction at the cathode both as an undissociated molecule and a singly charged anion, though, of course, at different potentials. With further increase in pH value, the first wave disappeared as the amount of undissociated molecules became insignificant.

TABLE 9

pH	Citraconic acid		Mesaconic acid	
	$E_{1/2}$ theor.	$E_{1/2}$ exp.	$E_{1/2}$ theor.	$E_{1/2}$ exp.
0.02		−0.61		−0.68
1.14	−0.65	−0.68	−0.72	−0.72
2.55	−0.76	−0.80	−0.83	−0.88
3.38	−0.81	−0.81	−0.88	−0.92
5.42	−0.93	−0.92	−1.00	−0.98
6.62	−1.00	−1.17	−1.07	−1.21
7.50	−1.05		−1.12	
8.00	−1.08		−1.15	

This is one explanation of the phenomenon. On the other hand, this phenomenon may be explained by a different mechanism of hydrogen addition to an organic molecule in acidic and alkaline media [25].

The calculated half-wave potentials of trans-cinnamic acid agree quite well with those found experimentally in all the pH range investigated (Table 10). This fact may be explained by the reduction of cinnamic acid molecules and not of its anions, due to the low value of the dissociation constants of the acid ($3.6 \cdot 10^{-5}$) at all pHs.

3. The graphs of the ratio of $\lg \frac{i}{i_d - i}$ to E are straight lines with $\lg \alpha = 0.59$ for citraconic, 0.73– – for mesaconic, 0.65 – for cis-aconitic, 0.53 – for trans-aconitic, 0.36 – for cis-cinnamic, 0.125 – for trans-cinnamic, 0.14 – for isocrotonic and 0.36– for crotonic acid.

Thus, $\alpha < 1$ for all the acids investigated, which indicates the irreversibility of their reduction at a dropping mercury cathode. The values for $E_{1/2}$ found graphically correspond quite well with those found experimentally (Table 11).

4. Although the processes investigated were, apparently, irreversible, we made the assumption that two electrons participated in the reduction of the acids (based on the dependence of $E_{1/2}$ on pH), i. e., the processes proceeded by the scheme

$$R + 2e + 2H \rightarrow RH_2.$$

In this case, substituting all the values found experimentally and n = 2 in Ilkovich's equation

$$i_d = 605\ nD^{1/2}\ cm^{2/3} t^{1/6},$$

we were able to calculate the diffusion coefficients of these acids.

TABLE 10

pH	Trans-cinnamic acid	
	$E_{1/2}$ theor.	$E_{1/2}$ exp.
0.02		—1.21
1.14	—1.28	—1.29
2.00	—1.38	—1.37
3.00	—1.39	—1.38
4.00	—1.45	—1.41
5.00	—1.51	—1.56
6.05	—1.57	—1.59
6.90	—1.62	—1.66
8.20	—1.69	—1.67

TABLE 11

Acids	$E_{1/2}$ graph (V)	$E_{1/2}$ exp. (V)
Citraconic	—0.755	—0.75
Mesaconic	—0.965	—0.96
Cis-aconitic	—0.625	—0.63
Trans-aconitic	—0.820	—0.82
Cis-cinnamic	—1.480	—1.51
Trans-cinnamic	—1.550	—1.56
Isocrotonic	—1.550	—1.57
Crotonic	—1.620	—1.60

TABLE 12

Acids	Indifferent electrolyte	Solvent	$D \cdot 10^6$ cm^2 · sec^{-1}
Citraconic	1 N HCl	75% alcohol	2.02
Mesaconic	1 N HCl	75 „ „	1.25
Cis-aconitic	1 N HCl	50 „ „	0.61
Trans-aconitic	1 N HCl	50 „ „	1.63
Cis-cinnamic	0.1 N NH_4Cl	50 „ „	0.31
Trans-cinnamic	0.1 N NH_4Cl	50 „ „	1.74
Isocrotonic	0.1 N NH_4Cl	Water	2.79
Crotonic	0.1 N NH_4Cl	„	3.13

We obtained the values given in Table 12. These values are quite probable if one considers the effect of the electrolyte and solvent present. For a comparison we should note that the diffusion coefficients, determined by other methods in a pure aqueous medium, according to the literature data, were found to be equal to: $8.2 \cdot 10^{-6}$, for succinic, $6.6 \cdot 10^{-6}$ for tartaric, $4.8 \cdot 10^{-6}$ sec^{-1} for citric acid, i.e., they have values of the same order as those of the coefficients we found.

SUMMARY

1. We investigated the polarographic behavior of four pairs of geometrically isomeric organic acids in relation to the background pH and the nature of the solvent. It was established that the polarographic behavior of the acids was considerably affected by the substitution of aqueous alcohol and alcohol media for the aqueous medium: the half-wave potential and diffusion current changed with this substitution and the changes were of an individual character. We explained the formation of two waves on the polarographic curves in a certain range of pH values of citraconic, mesaconic and both aconitic acids. We concluded that the reduction of the acids investigated was irreversible and that two electrons participated in it. The diffusion coefficients for these acids were calculated.

2. It was established that cis-isomers were reduced more readily at a dropping mercury cathode, i. e., at a less negative potential than trans-isomers.

3. We proposed methods for the quantitative polarographic determination of cis- and trans-isomers when both are present in solution.

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CATALYTIC CONVERSIONS OF PENTENE-1

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The thermal and catalytic conversions of pentene-1 described in the literature are, for the most part, concerned with investigating the composition of the equilibrium mixtures of pentenes, obtained as a result of shifting the double bond and isomerizing the skeleton of the molecule.

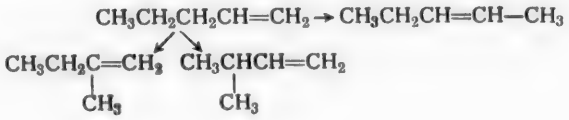
Thus Ewell and Hardy [1], studying the conversions of pentene-1 and pentene-2 on active aluminum oxide and various mixed catalysts, established that in the same contact time (12 hours) with aluminum oxide at 357°, pentene-1 was converted into pentene-2 to 78.1% and that at 358° the latter, in its turn, formed a mixture containing 15.8 of pentene-1 and 84.2% of pentene-2. In treating pentene-2 with alumomanganese and alumochromium catalysts at 305 and 295°, 10.7% and 11.8% of pentene-1 respectively, was obtained. D. N. Zharkova and B. L. Moldavsky [2], studying the composition of equilibrium mixtures of pentenes at 200 and 380°, confined themselves to showing that aluminum oxide, aluminum sulfate and phosphoric acid do not isomerize normal into branched pentenes. Schuit, Hoog and Verheus [3] investigated conversions of pentenes over permutite at 400° with a 33 second contact time. In three experiments with isopentene/pentene ratios of 4.0 and 1.5 in the starting mixture, they obtained a final mixture in which the ratio of these pentenes was 2.48, 4.56 and 2.08, respectively. Egloff, Morrell, Thomas and Bloch [4] observed the isomerization of pentene-1 into pentene-2 and methylbutenes in the moment of its formation in the dehydration of n-amyl alcohol over aluminum oxide at 400°; here 53% isomerization of the skeleton occurred. It was noted that isomerization of pentene-1 into pentene-2 occurred on an adsorbing catalyst of the brucite type, previously activated at 1000° F to remove water [5]. The isomerization of pentene-1 and pentene-2 on various forms of aluminum oxide was studied in detail by Oblad, Messenger and Brown [6], who carried out experiments in the vapor phase over a wide range of temperatures (177–427°) and volume rates (0.5–24 hours^{-1}). Of the two forms of aluminum oxide, which were treated with 5% hydrofluoric acid, the most active catalyst was prepared from the technical oxide. They established that isomerization of the hydrocarbon skeleton occurred mainly on acid catalysts; while neutral aluminum oxide mainly shifted the double bond, so that each of the isomerization processes has its own specific and conversion mechanism. Shifting of the double bond was also observed at lower temperatures. Thus, on using 70% sulfuric acid as catalyst at 170° F, a mixture of normal pentenes was formed from pentene-1 [7]. A most unusual result was obtained by Shatenshtein, Vasilev, Dykhno and Izrailevich [8]. In observing the conversion of pentene-1 in the presence of potassium amide in deuterated liquid ammonia, these authors obtained a hydrocarbon with b. p. 36° and n_D^{20} 1.3810, i.e., pure pentene-2. Thus, the complete conversion of pentene-1 into pentene-2 occurred at the boiling point of liquid ammonia. Meanwhile, comparing the free energies of formation of pentene-1 and pentene-2, it is readily seen that over a wide temperature range, they differ by approximately 1 kcal, and due to this the value of the logarithm of the constant is considerably less than unity, while the equilibrium concentration of pentene-1 in the mixture is never equal to zero. This conclusion is confirmed, in particular, by experiment [1, 2]. Kilpatrick, Prosen, Pitzer and Rossini [9] calculated the thermodynamic functions of pentenes and, from the values they obtained, estimated the equilibrium constants and the compositions of equilibrium mixtures of the series of reactions considered and showed that the results they obtained were confirmed, in the best way possible, by the experimental data of Ewell and Hardy [1].

Several investigations were devoted to thermal conversions of pentene-1. Thus, Norris and Thomson [10] established that thermal cracking of pentene-1 begins at 389°. The presence of traces of moisture considerably increases the rate of cracking. On passing the vapor of pentene-1 through a tube heated to 500–600°, it was found [11] that, as with pentene-2 also, more than half was cracked to form methane, butene-1, propene,

ethane and ethene in the molar ratios 6: 2: 2: 2: 1, respectively; small amounts of butene-2, butadiene and hydrogen were also formed. Molera and Stubbs [12] investigated the kinetics of thermal decomposition of pentene-1 at 480° as a function of pressure. They found that the rate of cracking increased with an increase in pressure. The activation energy of decomposition in the region of 430–530° at 100 mm Hg equalled 53.1 kcal/mole and at 300 mm – 54.6 kcal/mole.

It seemed interesting to us to investigate the conversions of pentene-1 on different catalysts and from a detailed analysis of the catalyzates, examine the possibility of the reaction proceeding not only to the isomerization of this alkene, but also to the disproportionation of hydrogen with the formation of the corresponding diene and alkane, as could be expected from the work of A. A. Petrov, Jr. and A. V. Frost [13]. As catalysts we used magnesium silicate ($2MgO \cdot SiO_2$), sinc silicate ($2ZnO \cdot SiO_2$), the mineral andalusite ($Al_2O_3 \cdot SiO_2$), zinc oxide, manganous oxide and platinum on silica, which had not been investigated previously in conversions of pentenes, and silica gel, which had been investigated previously [2].

The conversions described below were carried out at 300, 400, 450 and 500° at a constant volume rate of 0.1 hours^{-1}. We established that even at 300° pentene-1 is partially isomerized into pentene-2 and isomerization of its skeleton to form 3-methylbutene-1 and 2-methylbutene-1 only occurs to an insignificant degree.



The formation of 2-methylbutene-2 was observed neither at 300° nor at higher temperatures on all the catalysts investigated. The only exception was platinum on silica gel and in contact with this pentene-1 was converted into a mixture of hydrocarbons, from which we isolated 2-methylbutene-2 (b. p. 38°) in the individual state, as is shown by distillation data.

The activity of the silicate catalysts increases in the series andalusite → zinc silicate → magnesium silicate. Thus, from pentene-1 at 300° on andalusite we obtained 4.3% of pentene-2, on zinc silicate – 21.6% and on magnesium silicate–31.7%. With an increase in temperature, however, this rule does not show up so distinctly, apparently, as a result of the superposition of a series of other reactions.

On raising the temperature, the disproportionation of hydrogen begins to predominate, together with cracking. Here we noticed that not only acid catalysts had a capacity for disproportionating hydrogen, but also oxides, which did not have an acidic character. Thus, at 450° on andalusite and silica gel, there was an unsaturated hydrocarbon content of 49.4 and 43.4% in fractions with b. p. 20 – 29° and 34 – 36.5° respectively; on the other hand, on manganous oxide there were 69.3 and 89.1% unsaturateds in fractions 22.5 – 29° and 34 – 36.5°.

EXPERIMENTAL

Pentene-1 was prepared by the two following methods:

a) $C_2H_5MgCl + CH_2=CH-CH_2Cl \rightarrow CH_3-CH_2-CH_2-CH=CH_2 + MgCl_2$

b) $C_4H_9MgBr \xrightarrow{CH_2O} C_5H_{11}OH \xrightarrow{(CH_3CO)_2O} C_5H_{11}OOCCH_3 \xrightarrow{\text{pyrolysis}}$

$\rightarrow CH_3-CH_2-CH_2-CH=CH_2 + CH_3COOH$

In both cases the reaction product was distilled on a column with an efficiency of 30 theoretical plates and had the following properties: b. p. 29.5–30.3° at 754 mm, d_4^{20} 0.6425, n_D^{20} 1.3720. Literature data for pentene-1 [14]: b. p. 30.1°, d_4^{20} 0.6420, n_D^{20} 1.3711.

The yield of pentene-1 by scheme (a) was 65% and with an n-amyl alcohol yield of 70% of theoretical*; the yield of pentene-1 by scheme (b) did not exceed 30%, based on the starting alcohol.

The andalusite was broken into small pieces and heated with 30% sulfuric acid on a water bath, after which it was carefully washed with distilled water.

Magnesium and zinc silicates were prepared by carefully grinding in a mortar freshly precipitated magnesium and zinc hydroxides and freshly prepared silica gel, using a molar ratio of 2 : 1. Then the catalysts were formed into little cylinders and dried at 150°.

Manganous oxide was prepared by precipitating manganese nitrate with 25% ammonia. After washing, the precipitate was formed into little cylinders and dried at 150°. The manganous oxide was prepared by reducing the mixture of manganic oxide and manganese dioxide in a catalytic tube with hydrogen, while the temperature was gradually raised to 450°.

The silica gel was prepared by passing a current of carbon dioxide through a solution of sodium silicate and was then carefully washed. The gel was pressed out, formed into little cylinders and dried at 150°

Platinum on silica gel was prepared by soaking 40 g of the latter in a dilute solution of chloroplatinic acid and then reducing with hydrogen, while the temperature was gradually raised to 450° over a period of 5 hours. The catalyst contained 3% of finely dispersed platinum.

Experimental method. The catalytic conversions of pentene-1 were investigated in a flow system by the usual method.

TABLE 1

Cracking Action of Catalysts

Expt. No.	Catalyst	Experiment temperature	Amount of pentene-1 passed through (in g)	Catalyzate obtained (in g)	Degree of cracking (in %)
1	Andalusite	300°	30.0	29.2	2.5
2		400	27.6	22.0	20.5
3		450	50.0	38.0	24.0
4		500	50.0	36.0	28.0
5	$2MgO \cdot SiO_2$	300	50.0	46.0	8.0
6	$2MgO \cdot SiO_2$	450	50.0	44.0	12.0
7	$2MgO \cdot SiO_2$	500	50.0	25.0	50.0
8	$2ZnO \cdot SiO_2$	300	50.0	47.5	5.0
9	MnO	450	50.0	45.0	10.0
10	SiO_2	450	37.0	25.0	32.2
11	$Pt—SiO_2$	400	33.0	25.0	24.3

The temperature in the reaction zone was determined with a chromelalumel thermocouple. The pentene-1 was introduced into the catalytic tube from a burette at a constant volume rate of 0.1 $hours^{-1}$. The reaction products were trapped in a receiver, cooled in ice water, and a trap in a mixture of dry ice and methyl alcohol. The catalyzate was weighed and distilled on a column with a fractionating capacity of 30 theoretical plates. The degree of cracking was determined from the yield of liquid catalyzate. Each of the fractions obtained was analyzed for unsaturated hydrocarbon content by Kaufmann's method. In addition, the specific gravity and refractive index was determined for all the fractions. The results obtained are given in Tables 1 – 7.

* A method of preparing primary alcohols, which gives such high yields, was described previously [15].

TABLE 2

Expt. No.	Boiling point	Weight (in g)	Yield (in % of the original hydrocarbon)	d_4^{20}	n_D^{20}	Bromine number	Content of unsaturateds (in %)
			400°				
1	28—29°	1.7	6.1	0.6380	1.3720	220.0	99.6
2	29—30.5	5.8	21.0	0.6384	1.3740	228.1	100.0
3	30.5—34	2.6	9.4	0.6400	1.3795	221.5	97.9
4	34—36.5	4.0	14.5	0.6519	1.3818	220.0	98.1
	Residue > 36.5	2.2	8	—	—	—	—
			450°				
1*	19—29	2.1	4.2	0.6292	1.3616	112.6	49.4
2	29.0—30.5	16.5	33	0.6410	1.3700	220.3	97.2
3	30.5—34	6.1	12.2	0.6408	1.3700	197.3	87.6
4**	34—36.5	7.6	15.2	0.6397	1.3793	177.2	81.9
5***	36.5—40	0.5	1.0	—	—	286.0	125% (double bonds)
6****	40—50	1.1	2.2	—	—	253.2	110% (double bonds)
	Residue	4.1	8.2	—	—	—	-
			500°				
1	26—29.0	3.1	6.2	0.6282	1.3609	103.6	45.4
2	29.0—30.5	10.9	21.8	0.6380	1.3684	177.2	77.7
3	30.5—34.0	3.2	6.4	0.6383	1.3685	169.1	74.5
4	34.0—36.5	4.6	9.2	0.6375	1.3691	161.4	70.7
5	36.5—40.0	1.8	3.6	0.6476	1.3840	180.1	78.8
6	40—50.0	1.3	2.6	0.7010	1.3965	189.2	78.4
7	50—60.0	2.6	5.2	0.7089	1.4015	124.3	—
	Residue	11.4	22.8	—	—	—	—

* Fraction contains 2-methylbutane.

** Contains n-pentane.

*** Contains a significant amount of diene.

**** Contains diene.

TABLE 3

Properties of Fractions, Isolated From Catalyzates of Pentene-1 at 450 and 500° in Experiments with $2MgO \cdot SiO_2$

Fraction No.	Boiling point of fractions	Weight (in g)	Yield (in % of the original pentene-1)	d_4^{20}	n_D^{20}	Bromine number	Content of unsaturateds (in %)
			450°				
1	22—20°	2.0	4.0	0.6379	1.3723	221.4	96.9
2	29—30.5	16.0	32.0	0.6412	1.3715	230.0	100.8
3	30.5—34.0	1.8	3.6	0.6407	1.3740	225.3	98.7
4	34.0—36.5	9.1	18.1	0.6400	1.3701	185.6	81.2
5	36.5—40	4.2	8.4	0.6615	1.3883	225.7	99.4
6	40—50	2.8	5.6	0.6719	1.3900	220.0	96.3
7	Residue	7.7	15.4	—	—	—	—
			500°				
1	20—29	2.2	4.4	0.6385	1.3692	178.8	78.0
2	29—30.5	8.0	16.0	0.6404	1.3710	193.2	84.5
3	30.5—34	0.8	1.6	0.6410	1.3713	182.1	79.7
4	34—36.5	4.9	9.8	0.6427	1.3751	174.2	76.3
5	Residue	4.1	8.2	—	—	—	—

TABLE 4

Conversion Products of Pentene-1 in Contact with MnO at 450°

Fraction No.	Boiling point of fractions	Weight of fraction (in g)	Yield (in % of the original pentene-1)	d_4^{20}	n_D^{20}	Bromine number	Content of unsaturateds (in %)
1	22.5—29.0°	3.1	6.2	0.6358	1.3632	158.8	69.3
2	29.0—30.5	23.7	47.2	0.6412	1.3650	192.8	84.3
3	30.5—34.0	0.7	1.4	—	1.3698	203.3	89.1
4	34.0—36.5	1.3	2.6	—	1.3720	203.3	89.1
5	36.5—40.0	1.7	3.4	—	1.3762	—	—
6	40.0—50.0	2.7	5.4	0.6708	1.3890	182.4	79.5
7	Residue	11.0	22.0	—	—	—	—

TABLE 5

Conversion Products of Pentene-1 in Contact with SiO_2 at 450°

Fraction No.	Boiling point of fractions	Weight of fraction (in g)	Yield (in % of the original pentene-1)	d_4^{20}	n_D^{20}	Bromine number	Content of unsaturateds (in %)
1	20—29.0°	1.6	4.3	0.6371	1.3720	99.2	43.4
2	29.0—30.5	3.4	9.2	0.6420	1.3730	142.2	62.3
3	30.5—34.0	1.1	3.0	—	1.3780	185.6	81.3
4	34.0—36.5	13.5	36.6	0.6446	1.3833	214.0	94.0
5	36.5—40.0	0.7	1.9	—	1.3912	—	—
6	40.0—50.0	0.7	1.9	0.6882	1.3922	174.6	76.5
7	Residue	4.0	10.9	—	—	—	—

TABLE 6

Conversion Products of Pentene-1 in Contact with $Pt-SiO_2$ at 400°

Fraction No.	Boiling point of fractions	Weight of fraction (in g)	Yield (in % of the original pentene-1)	d_4^{20}	n_D^{20}	Bromine number	Content of unsaturateds (in %)
1	20—29°	8	24.2	0.6412	1.3710	220.8	96.7
2	29.0—30.5	1.2	3.6	—	1.3720	221.3	97.8
3	30.5—38.0	5	15.2	0.6600	1.3813	224.0	98.2
4	38.0	5	15.2	0.6615	1.3878	226.6	99.2
5	38.0—50.0	2.9	8.7	0.6714	1.3912	229.5	100.6
6	Residue	2.9	8.7	—	—	—	—

In experiments in contact with andalusite at 300, 400, 450 and 500°, the following results were obtained. At 300° the unchanged pentene-1 was 67.1% (20.1 g) of the original; fractions with b.p. 30.5-34, 34-36.5, 36.5-50° at 754 mm comprised respectively 3.5, 4.3 and 8.5% and the residue —8.1%. Fractions obtained from the catalysts at 400, 450 and 500° are given in Table 2.

From the conversion products of pentene-1 in contact with $2MgO \cdot SiO_2$ at 300°, we isolated 0.6 g (1.2%) of a fraction with b.p. 27-29°, a bromine number of 223.3 and an unsaturateds content of 97.5%; 40% consisted of unchanged pentene-1 and 31.7% of pentene-2. We also isolated fractions 36.5-40° and 40-50°, which amounted to 3.4 and 2.8%, respectively, of the starting pentene-1 and had bromine numbers of 229.2 and 224.1, corresponding to 100 and 98% unsaturateds contents.

The results obtained in experiments with these catalysts at 450 and 500° are given in Table 3.

TABLE 7

Conversion Products of Pentene-1 in the Presence of $2ZnO \cdot SiO_2$ at 300°

Fraction No.	Boiling point of fractions	Weight of fraction (in g)	Yield (in % of the original pentene-1)	d_4^{20}	n_D^{20}	Bromine number	Content of unsaturateds (in %)
1	29—30.5°	23.8	47.6	0.6403	1.3730	220.8	96.7
2	30.5—34.0	7.6	15.2	0.6432	1.3740	221.3	97.8
3	34.0—36.5	10.8	21.6	0.6439	1.3812	226.6	99.2
4	36.5—40.0	1.2	2.4	—	1.3856	228.5	99.5
5	40.0—50.0	0.9	1.8	—	1.3864	229.5	100.6
6	Residue	3.2	6.4	—	—	—	—

SUMMARY

1. We investigated the conversion of pentene-1 in contact with andalusite, zinc and magnesium silicates, manganous oxide, silica gel and platinum on silica gel, at various temperatures (300–500°).

2. It was shown that under the given conditions, the isomerization of pentene-1 into pentene-2 mainly occurred; at the same time, isomerization of the skeleton and disproportionation of hydrogen occurred with the formation of small amounts of dienes and pentanes.

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ESTERS OF BORIC ACID IN THE FRIEDEL - CRAFTS REACTION

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The use of esters (sulfates, carbonates, silicates, phosphates, hypochlorites etc.) as alkylating agents in the Friedel-Crafts reaction is described in the literature [1–5]. These reagents are convenient, especially in those cases when the alkenes or alkyl halides usually used are difficultly accessible or give poor results in the alkylation with aluminum chloride, usually due to side reactions.

Two of the authors have used esters of boric acid for the alkylation of aromatic hydrocarbons in the presence of aluminum chloride [6]. In the present work we continued this investigation and widened it, using chlorobenzene and phenol as well as aromatic hydrocarbons as compounds for alkylation.

The results of the experiments are given in Table 1. It is noteworthy that on increasing the molecular weight of the alkyl, the yield does not decrease and that the alkylation of aromatic compounds with boric esters of normal primary alcohols proceeds with good yields, in contrast to alkylation with alcohols [7, 8] and various esters of other inorganic acids [1-5] where the yields fall sharply on increasing the molecular weight of the alcohol. In these cases, alkylation with boric esters is convenient as a preparative method, particularly as the boric esters are readily prepared and in good yield [9]. In the present work we succeeded in preparing triethyl borate by esterification (in a Dean and Stark apparatus) and also prepared the boric ester of 2-ethylhexanol-1 for the first time.

From the alkylation reaction equation

$$3ArH + B(OAlk)_3 + AlCl_3 \xrightarrow{AlCl_3} 3Alk—Ar + 3HCl + AlBO_3$$

it is obvious that one mole of boric ester requires more than the molar amount of aluminum chloride; one mole is used as a reagent and the rest acts as a catalyst.

In studying the alkylation of benzene with tributyl borate, we found (Table 2) that decreasing the amount of aluminum chloride led to a decrease in the yield of butylbenzene, while increasing it led to an increased amount of high-boiling products and an increase in tar formation, so that the amount of monoalkylated product also decreased. A special experiment, which is not described, showed that the amount of hydrogen chloride liberated was equimolecular to the butylbenzene obtained, in agreement with the reaction equation. By distilling the mixture of butylbenzenes on a Vigreaux column 60 cm high, we isolated 86.8% of sec-butylbenzene.

TABLE 2

Amount (moles) of aluminum chloride per mole of tributyl borate	Yield of butylbenzene (in %)
0.15	0.0
1.0	37.0
1.2	59.0
1.5	77.7
2.25	58.0
3.0	47.6

A similar isomerization, usual for alkylation in the presence of aluminum chloride, also occurs in other cases - for example n-propyl and isobutyl boric esters form isopropylbenzene and tert-butylbenzene, respectively.

We found that in a reaction between tripropyl borate and aluminum chloride under the same conditions, as in experiment 3, Table 1, alkyl halides were not formed. Neither were they formed on heating tributyl borate with aluminum chloride to 200°. As shown by a special experiment, hydrogen chloride does not break down butyl borate and other boric esters, i. e., alkyl chloride cannot

TABLE 1

Experiment No.	Boric ester (0.05 mole)	Amount of aluminum chloride (in moles)	Amount of compound to be alkylated* (in g)	Reaction conditions: Time (in hours)	Reaction conditions: Temperature	Name	Reaction products: Yield: g	Reaction products: Yield: as % of theoretical, calculated on the ester	Reaction products: Boiling point	Reaction products: Boiling point after second distillation	Literature
1	Ethyl	0.075	117	5	80—82°	Ethylbenzene	7.15	45.0	115—145°	135—137°	[11]
2	n-Propyl	0.0675	156	5.5	60—75	Isopropylbenzene	11.9	66.1	125—170	150—152.5	[11, 12]
						Diisopropylbenzenes	1.6	13.1	170—220		
3	Isopropyl	0.0575	117	7.5	50—70	Isopropylbenzene	14.2	78.2	125—170	151—154	[11, 12]
						Diisopropylbenzenes	0.5	4.1	170—220		
4	n-Butyl	0.075	117	5	80—86	sec-Butylbenzene	15.6	77.6	140—200	171.5—173	[11, 12]
						Dibutylbenzenes	1.1	7.7	200—240		
5	Isobutyl	0.0665	156	5	40—65	tert.-Butylbenzene	11.0	54.7	140—200	168—170	[11, 12]
				1	70—75	Dibutylbenzenes	1.6	11.2	200—240		
6	Isobutyl	0.075***	58	14.5	86—88	tert.-Butylbenzene	6.0	29.9	140—200	168—170	[11, 12]
						Dibutylbenzenes	1.4	9.8	200—240		
7	Isoamyl	0.075	156	6	50—75	tert.-Amylbenzene	13.8	62.1	155—220	188.5—190	[11, 12]
				0.5	80	Diamylbenzenes	2.5	15.2	220—260		
8	Isooctyl (2-ethyl-hexanol-1)	0.0825	58	9	80—85	3-Methyl-3-phenylheptane	12.6	44.2	220—260	120—122(17)	[11]
						Dioctylbenzenes	1.6	7.9	260—290		
9	Octyl (octanol-2)	0.075	117	9.5	80—85	Sec-octylbenzene	19.2	67.3	220—250	241—244	[11]
10	Cyclohexyl	0.055	156	5	35—45	Cyclohexylbenzene	18.6	77.5	90—98(5)	95—96(5)	[11, 13]
				2	60—80	Dicyclohexylbenzenes	2.7	14.9	100—130(5)		
11	Benzyl	0.055	117	18	25—32	Diphenylmethane (m.p. 26-27)	18.1	71.8	95—103(3.5)	100—102(3.5)	[11]
						Dibenzylbenzenes	2.8	14.6	103—120(3.5)		
12	Allyl	0.075	156	12	60—65	Diphenylpropane	13.6	46.2	135—175(14)	281—283	[11, 14]
				1	75	Isopropylbenzene	3.1	17.1	150—165	155—156	
13	Ethylene glycol	0.15	156	11.5	80	Dibenzyl (m.p. 51-52°)	7.0	25.6	270—285	281—283	[11, 16]
14	ω-Chloroethyl	0.15	156	12	75	Dibenzyl	22.5	82.4	270—285	281—283	[11, 16]
15	ω-Chloroethyl	0.15	184	11	84—94	Ditolylethane-1,2	24.5	77.7	155—170(10)	163—164(10)	[11—15, 18]

TABLE 1 (Cont'd.)

Experiment No.	Boric ester (0.05 mole)	Amount of aluminum chloride (in moles)	Amount of compound to be alkylated* (in g)	Reaction conditions: Time (in hours)	Reaction conditions: Temperature	Name	Reaction products: Yield g	Reaction products: Yield as % of the theoretical, calculated on the ester	Reaction products: Boiling point	Reaction products: Boiling point after second distillation	Literature
16	Allyl	0.075	184	8.5	45—55	1,2-Ditolylpropane	19.5	58.0	130—150(3)	138—140(3)	[11, 17]
17	β-Chloroethyl	0.150	212	11	85—96	1,2-Dixylylethane	29.0	81.2	135—145(3)	142—143(3)	[6]
18	n-Butyl	0.0925	112.5	5	80—86	p-sec-Butylchlorobenzene****	17.2	68.1	190—270	208—210	[21]
						Dibutylchlorobenzenes	1.1	6.5	230—270		
19	Isoamyl	0.075	112.5	6	64—76	p-tert.-Amylchlorobenzene****	12.0	43.8	195—240	227—229	[18, 20]
				6	80—86	Diamylchlorobenzenes	5.1	26.8	240—280		[22]
20	n-Butyl	0.100	14.1	4.5	90—100	o-sec-Butylphenol	11.6	51.5	225—250	230—232	[19, 21, 22]
				0.5	110—130	p-sec-Butylphenol				240—243	
21	n-Butyl	0.125	14.1	6	100	o-sec-Butylphenol	11.7	52.0	225—250	230—232	[21, 22]
						p-sec-Butylphenol				240—243	
22	n-Butyl (0.072 mole)	0.160	14.1	6	100	o-sec-Butylphenol	12.2	54.0	225—250	230—232	[21, 22]
						p-sec-Butylphenol				240—243	
						Dibutylphenols	2.7	18.6	260—280		

* Compounds alkylated in experiments 1-14 – benzene, in 15-16– toluene, 17 – m-xylene, 18, 19 – chlorobenzene, 20, 22 – phenol.

** On oxidizing, we obtained benzoic acid with m.p. 121°.

*** Experiment with ferric chloride as catalyst.

**** By oxidation we obtained p-chlorobenzoic acid with m.p. 239-240°.

be formed in this way either. In the literature there are reports that alkyl halides, also, are not obtained in the reaction of aluminum chloride with diethyl sulfate, diethyl carbonate and isopropyl acetate [2, 3].

If, after hydrolysis of the reaction mixture and separation of the hydrocarbons, the aqueous layer, containing aluminum borate, is evaporated down and acidified to congo with sulfuric acid, the boric acid precipitates and may be used repeatedly for the synthesis of boric esters. The aluminum sulfate formed does not interfere with the esterification of boric acid. The esterification does not proceed directly (without acidification with sulfuric acid), i. e., the reaction mixture does not contain free boric acid. Chemically pure aluminum borate specially used for this purpose also gave esters of boric acid only after acidification with sulfuric acid.

We found that benzene was not alkylated with alkyl halides in the presence of aluminum borate; saturation of this mixture with hydrogen chloride, also, did not promote alkylation.

In alkylating aromatic hydrocarbons with boric esters of allyl alcohol and ethylene chlorohydrin, we obtained good yields of the di-substituted derivatives, namely 1, 2-diphenylpropane and dibenzyl, respectively, from benzene. We investigated the condensation of triallyl borate with benzene at temperatures from − 5° to + 80° with various amounts of aluminum chloride; we obtained hardly any monosubstituted products − allylbenzene or 2-phenylpropyl alcohol. In condensing tri-β-chloroethyl borate with benzene, we also were unable to obtain monosubstituted derivatives − phenylethyl alcohol or β-chloroethylbenzene (cf. [10]).

If in alkylating benzene with isobutyl borate, the aluminum chloride was substituted by ferric chloride (Table 1, Experiment 6), the reaction time increased and the yield decreased. Phosphorus pentoxide was not suitable as a catalyst for this reaction. Using ferric chloride as a catalyst in the condensation of tri-β-chloroethyl borate with benzene gave a negative result.

We were unable to arylate benzene with triphenyl borate. After boiling a mixture of triphenyl borate and benzene for many hours in the presence of aluminum chloride, we only isolated benzene and phenol from the reaction mixture.

In alkylating chlorobenzene with boric esters, the p-isomer was mainly obtained; oxidation of the alkylchlorobenzenes obtained gave p-chlorobenzoic acid. Butylation of phenol with equimolecular amounts of tributyl borate gave predominantly p-sec-butylphenol. Increasing the amount of aluminum chloride did not affect the yield (Table 1, Experiments 20 and 21). The use of excess tributyl borate lead to a small amount of dibutyl phenols (Table 1, Experiment 22).

We also tested aluminum alcoholates as alkylating agents. On heating aluminum ethylate with benzene for many hours, even in the presence of a large amount of aluminum chloride $AlCl_3 : Al(OC_2H_5)_3 = 3:1$, we obtained ethylbenzene in a 47.2% yield and diethylbenzene in a 4.6% yield. We did not obtain alkylation products with methyl and n-propyl aluminates.

EXPERIMENTAL

Synthesis of triethyl borate. A mixture of 50 ml (0.86 mole) of ethyl alcohol, 70 ml of benzene, 15.5 g (0.25 mole) of boric acid and 5 g of anhydrous copper sulfate was boiled in a Dean and Stark apparatus until water no longer distilled off (azeotropic mixture), which practically was 40-50 hours. Then the reaction mixture was distilled with a pear fractionating column 15 cm high, collecting the fraction 100-128°. The yield was 13.2 g (36%). After redistilling, we obtained 10 g of triethyl borate with b. p. 117-120°, d_4^{20} 0.8660, n_D^{20} 1.3775.

Found %: B 7.03, 7.00. $C_6H_{15}O_3B$. Calculated %: B 7.40.

Synthesis of the borate ester of 2-ethylhexanol-1. A mixture of 7.75 g (0.125 mole) of boric acid and 100 ml of 2-ethylhexanol-1 (b.p. 183-184°, n_D^{20} 1.4315) was boiled in a Dean and Stark apparatus. Over 3 hours the temperature of the reaction mixture rose from 110 to 198°; at this point water ceased to distil off. By distillation in vacuum we obtained 49.3 g (99%) of tri-(2-ethyl)-hexyl borate with b.p. 183-185° at 3 mm; d_4^{20} 0.8619, n_D^{20} 1.4385.

Found %: B 2.53, 2.63. $C_{24}H_{51}O_3B$. Calculated %: B 2.79.

Alkylation with boric esters was carried out in a three-necked, round-bottomed flask, fitted with a mechanical stirrer, a reflux condenser with a calcium chloride tube and a thermometer. In all cases, the boric ester and the compound to be alkylated were first mixed and then over 1 hour at 20-25°, the catalyst was added (in experiments with triallyl borate, over 3 hours). The reaction mixtures were heated on a water bath at the various temperatures given in Table 1. After the reaction, the mixture was cooled and was added to 150-200 ml

of cold water; the hydrocarbon layer was washed with a 3% solution of soda and the aqueous one extracted with ether. Both solutions were dried, mixed and distilled from a flask with a pear fractionating column 10 cm high. After a second distillation on a Vigreaux column 60 cm high, we isolated the pure monoalkylated derivatives. The constants agreed with literature data.

The effect of aluminum chloride on tripropyl borate. Into a three-necked, round-bottomed flask, fitted with a reflux condenser, a mechanical stirrer and a thermometer, was placed 9.4 g (0.05 mole) of tripropyl borate, 9 g (0.0675 mole) of aluminum chloride and 65 ml of nitrobenzene and the mixture stirred for 5 hours at 60-75°. The reaction mixture darkened, and after 2.5 hours became very thick and after a further hour it again became liquid. Hydrogen chloride was not evolved. On heating the reaction mixture to 90°, propyl chloride did not distil off.

SUMMARY

We studied the alkylation of benzene, toluene, m-xylene, chlorobenzene and phenol with esters of boric acid and showed the advantages of using it as a preparative method.

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CATALYTIC REACTION OF ETHERS WITH CARBOXYLIC ACIDS

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In addition to the existing catalytic methods already described in the literature for obtaining esters (liquid phase [1] and vapor phase [2], esterification of carboxylic acids with alcohols, esterification of carboxylic acids with olefins under pressure [3], and dehydrogenation of alcohols with subsequent ester condensation of aldehydes [4], we have proposed the possible production of esters by reaction of carboxylic acids with ethers according to the general equation

$$2RCOOH + (R_1)_2O = 2RCOOR_1 + H_2O$$

Nothing has yet been recorded in the literature on such a reaction. The purpose of the present work was to find the best catalysts and optimum conditions for the process. Thermodynamic analysis undertaken for reaction of dimethyl and diethyl ethers with different carboxylic acids [5] in the gas phase showed that equilibrium yield of the ester varied only slightly within the range 200-300°. With increase in the molar ratio $b = (C_2H_5)_2O : CH_3COOH$ from 1 : 1 to 7 : 1, the value of the equilibrium stage of acid conversion (α) increases. The value (α) is changed in this case from 0.7-0.75 to 0.9-0.93. Further increase of value b has practically no effect on value α. Reaction of dimethyl ether with formic acid is exceptional. In this case the equilibrium yield of methyl formate does not exceed 7-11%.

EXPERIMENTAL

The experiments were undertaken in a flowing system in a horizontal electric furnace with automatic heat control. It must be specially emphasized that reproducibility of results and normal flow of process in timed relation were achieved by preliminary saturation of the catalyst with ether vapor (dimethyl or diethyl). The initial components – dimethyl and diethyl ethers and also the acids: acetic, propionic, butyric – with constants corresponding to literature data were previously mixed and added to a pre-calculated rate. In esterifying the acids with the dimethyl ether, the latter is supplied from a gas-holder together with brine previously saturated with the dimethyl ether. Reading began with establishment of steady operating conditions. The reaction products passing through a condenser were condensed in the collector and trap, which were cooled with dry ice. The unreacted dimethyl ether residue is recovered with conc. H_2SO_4 (d 1.84). As a rule, gaseous products were not obtained, this indicating the absence of any decomposition of the simple ethers.

In the condensate were determined unreacted acid (by titration in the presence of phenolphthalein) and the ester (by washing with 1 N NaOH solution). Analysis results were checked by periodic distillation of the condensate. The esterification of acetic acid with diethyl ether and of acetic, propionic and butyric acids with dimethyl ether were studied.

The following were tested as catalysts: activated carbon of AR-3 brand (Sample 1), activated carbon impregnated with phosphoric acid up to 20% content (Sample 2), and up to 44% (Sample 3), also β-sulfonaphthalenic acid up to 26% (Sample 4); aluminosilicate of the Houdry type (Sample 5), aluminosilicate saturated with β-sulfonaphthalenic acid up to 13% (Sample 6) and up to 26% (Sample 7), and with sulfuric acid up to 20% (Sample 8); silicophosphoric acid (Sample 9)activated aluminum oxide (Sample 10), and silica gel impregnated with phosphoric acid up to 20% (Sample 11).

Catalyst samples 2, 3, 4, 6, 7, 8, 11 were prepared as follows. The carriers previously calcined for 1½ to 2 hours (activated carbon at 300-350°, aluminosilicate and silica gel at 400-450°) were quickly immersed in

an aqueous solution of the corresponding acids or salts. The volume of the solution in all cases ranged from 0.55 to 0.6 of the impregnated volume of carrier. In this way practically complete evaporation of water and penetration of acid (salt) into the pores of the carrier were ensured. Then the catalyst was placed in a contact oven and additionally dried in a nitrogen current for 2-4 hours at 120-200° (when using carbon as carrier) or 200-250° (with aluminosilicate). In tests with aluminosilicate (Sample 4) it was previously calcined for 1½ hour at 500°.

The silicophosphoric acid (Sample) was prepared as follows: to 8 ml of 79.4% hot phosphoric acid were gradually added, with continual mixing and heating, 15 g of infusorial earth (kieselguhr). The mass gradually thickened and darkened. Within 40-50 minutes with continual heating (200-250°) and stirring, it began to clear. Heating was continued for 2-2½ hours with constant rise in temperature up to 400-450° until complete clearing.

After cooling off in the vacuum drier, the catalyst was shaped into small balls and placed in the contact oven where it was activated with an air stream for 2 hours at 350°. The ratio $SiO_2 : P_2O_5$ in the catalyst was 1:1.

Catalytic Reaction of Diethyl Ether with Acetic Acid

The effect of temperature, ratio of diethyl ether : acetic acid, and time of contact on the yield of ethyl acetate was studied in using the catalyst – phosphoric acid on activated carbon (Sample 2). The results of the tests are shown in Figs. 1 and 2.

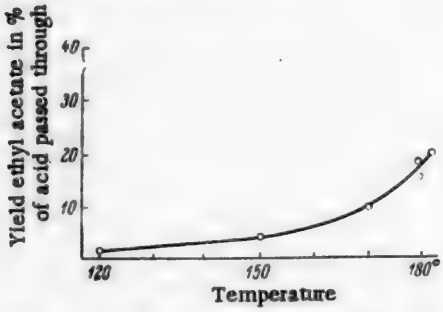

Fig. 1. Effect of temperature on yield of ethyl acetate, with molar ratio $(C_2H_5)_2O$: CH_3COOH = 1 : 1.

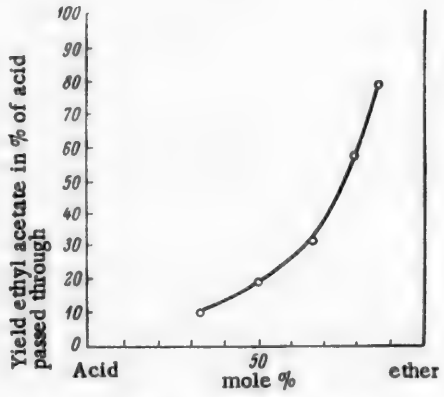

Fig. 2. Effect of ratio between $(C_2H_5)_2O$ and CH_3COOH on yield of ethyl acetate at 180°. Duration of tests 60 minutes, τ 25-30 seconds.

From the data of Figs. 1 and 2 it is evident that the yield of ethyl acetate increases with increase in temperature and in the ratio $(C_2H_5)_2O : CH_3COOH$ of initial mixture. Increase in time of contact (from 25 to 50 seconds) while maintaining a constant ratio $(C_2H_5)_2O : CH_3COOH$ = 6 : 1 only to a very insignificant extent raises the yield of ethyl acetate (from 78 to 84% at 180°).

Rise of temperature above 180° is inadvisable in view of the observed decomposition of the diethyl ether to ethylene. Tests lasting more than 100 hours showed that the activity of the catalyst (Sample 2) remains practically unchanged. Comparative data from study of activity of the other catalysts are given in Table 1.

From the data in Table 1 it is evident that the acids carried on activated carbon (phosphoric, β-sulfonaphthalenic) and aluminosilicate (β-sulfonaphthalenic, sulfuric), and also aluminosilicate itself, are sufficiently active catalysts of esterification of acetic acid with diethyl ethers. The yield of ethyl acetate reached 80-90% of the acid passed through. Zinc phosphate and acetate carried on activated carbon, as also activated carbon itself, have low activity. The activity of aluminosilicate decreases with time, but is fully restored after air-blowing the catalyst at 500-550° for 4-5 hours.

TABLE 1

Activity of Catalysts of Esterification of Acetic Acid with Ethyl Ethers (molar ratio of $(C_2H_5)_2O : CH_3COOH = 6:1$; time 1 hour

No. of catalysts	Temperature	Time of contact (sec)	Yield of ethyl acetate on acid passed (in %)
1	180°	30.8	12.5
4	180	7.8	42.8
	180	14.3	75.0
	180	30.1	86.5
3	155	15.9	46.2
	155	17.2	51.7
5	180	18.1	59.8
	200	9.6	69.5
	200	12.8	86.5
	200	19.2	89.8
6	120	18.1	69.3
7	180	17.5	73.7
8	130	22.6	81.5
	130	41.3	85.0

In using sulfuric acid on aluminosilicate as catalyst the optimum temperature is 130°. In the case of phosphoric acid on carbon (up to a content of 20%) the optimum temperature is 180°, with a content of 44% it is 155°, with β-sulfonaphthalenic acid on carbon and aluminosilicate it is 180°, and with pure aluminosilicate, 200°.

Catalytic Reaction of Dimethyl Ether with Acetic Acid

From the example of the reaction of dimethyl ether with acetic acid, the attempt was made to find the optimum conditions and also the most effective catalysts for the process. The relation was studied between yield of methyl acetate and temperature, volumetric rate of flow, and ratio of initial components on the above mentioned catalyst samples. Duration of tests in all cases was 1 hour; volume of catalyst 50 ml; rate of flow 0.5 liter/liter catalyst hr.

TABLE 2

Activity of Catalysts of Esterification of Acetic Acid by Dimethyl Ether

No. of catalyst	Temperature	Molar ratio ether : acid	Yield meth. acetate % of acid used		Remarks
			passed	react.	
2	200°	2:1	61.1	100	Vol. rate 1.0
	270	2:1	94.1	100	
	250	2:1	81.4	100	
	250	2:1	87.4	100	
9	250	2:1	48.8	97.6	Vol. rate 0.2
	270	2:1	74.0	99.5	
	200	4:1	54.6	98.1	
	230	4:1	82.0	100	
	250	4:1	95.7	97.8	Condensate slightly colored
5	250	4:1	51.4	94.9	
	270	4:1	63.8	96.3	
10	270	2:1	21.4	90.7	
	350	2:1	42.0	93.5	
	350	10:1	71.1	95.6	
11	270	2:1	4.7	98.4	

Results of tests with different catalysts are shown in Table 2.

From the data presented in Table 2 it follows that catalyst activity is determined by the nature of the carrier, as also by that of the substance carried. This is particularly well shown by comparison of activity of catalysts Nos. 2 and 11. Under the same conditions of test, in using phosphoric acid on activated carbon (AR-3 brand) the yield of methyl acetate reaches 94.1% reckoned on the acid used, whereas, when using phosphoric acid carried on silica gel, the yield is only 4.7%.

Increase of temperature and of ratio of dimethyl ether : acetic acid (with constant temperature) ensures a higher degree of conversion of acetic acid into ester. Change in volume rate of flow within the limits 0.2 to 1.0 only slightly lowers the yield of methyl acetate.

On comparing the results obtained in the production of methyl acetate with those in the production of ethyl acetate from diethyl ether and acetic acid, it is evident that, in the case of methyl acetate, the temperature should be higher by 70-90° than with ethyl acetate. This may be explained by the suggestion that dimethyl ether is more stable and more difficultly activated than the diethyl ether. The best catalyst for the process is Sample 2 (phosphoric acid on carbon AR-3). In this case the maximum yield is observed in respect to acid passed through and reacted. Therefore all further experimental work in the production of other methyl esters (methyl propionate, methyl butyrate) was undertaken with this catalyst.

Catalytic Reaction of Dimethyl Ether with Propionic and Butyric Acids

The effect was studied of temperature and ratio of dimethyl ether to acid on yields of methyl propionate and methyl butyrate. All the experiments were made with catalyst No. 2, the volume of which was 50 ml and volume rate 0.5. Results are given in Table 3.

TABLE 3

Production of Esters from Dimethyl Ether

Temperature	Molar ratio ether : acid	Yield of ester on acid (mole %)	
		Passed	Reacted
	Tests with propionic acid		
250°	2 : 1	65.1	78.0
270	7 : 1	72.2	83.7
	Tests with butyric acid		
230	7 : 1	46.4	55.5
250	7 : 1	64.4	78.5
270	7 : 1	67.5	83.2
300	7 : 1	70.0	85.7
270	2 : 1	60.2	80.3

TABLE 4

Ester yields in Reacting Dimethyl Ether with Acids

Name of compound	Molar ratio	Yield of ester % of acid	
		Passed	Reacted
Methyl acetate	2 : 1	94.1	100
Methyl propion.	2 : 1	69.6	81.9
Methyl butyr.	2 : 1	62.0	80.3
Methyl propion.	7 : 1	72.2	83.7
Methyl butyr.	7 : 1	67.5	83.2

Raising the temperature and the ratio of dimethyl ether to acid only slightly increases yield of methyl propionate (Table 3). With rise in temperature from 230° to 300° the yield of methyl butyrate increased from 46.4 to 70% on the acid passed through and from 55.5 to 85.7% on acid reacted.

Increase in the ratio dimethyl ether : butyric acid from 2 : 1 to 7 : 1 at 270° also favors an increase in yield of the methyl butyrate from 60.2 to 67.5% reckoned on the acid used, although from equilibrium data it should reach about 90%.

By comparing the results of contact esterification of different acids by dimethyl ether at 270° it is evident that, under equal conditions the yield of the corresponding ester declines with increase in mol. wt. of the acid (Table 4).

It must be noted that in the formation of methyl propionate and methyl butyrate the yield of ester based on reacted acid does not reach 100%, although no secondary reactions were observed under these conditions.

By analogy with other catalyzed acidic reactions we suppose that the limiting stage of the process of esterification of carboxylic acids with ethers is that of activation of the components inclusive in the polarization of the molecules by the proton of the acid – catalyst. There should be activation both of the acid and of the ether. In such case, in all probability, a ternary complex should be formed of catalyst – acid – ether, in which, as a result of redistribution of bonds, polarization by the catalyst proton occurs, with necessary formation of the end product – the ester.

Owing to the considerable dipole moment and the presence of the carboxylic bond, polarization of the acid molecule, through attraction thereby of a catalyst proton to the carboxylic acid, should be easier and quicker than that of the ether molecules.

In passing through a mixture of vapors of ether and acid, owing to the very probable formation of a binary complex, adsorption of acid will predominate over that of ether. The acid will be polarized more and the ether less than is required to effect the esterifying reaction. As a result of this there is deactivation of the catalyst, as we have also observed.

Therefore for normal running of the process excess of ether above the stoichiometric and also preliminary impregnation of the catalyst therewith are also essential. The presence of a large number of molecules of the ether on the catalyst surface does not, in this case, permit the acid to be polarized by the catalyst proton more strongly than is necessary to form the corresponding complex. Moreover, the conditions are created for formation of a ternary complex.

In view of the foregoing we can understand also the need for choosing a large excess of ether in proportion to the increase in molecular weight of the acid to be esterified. The heat of adsorption of acid vapors by the catalyst (λ) is the summated heats of acid condensation at the reaction temperature (λ_1) and of the heat of its reaction with the catalyst, involved in the transfer of a proton from the catalyst to the carboxyl oxygen of the acid (λ_2): $\lambda = \lambda_1 + \lambda_2$.

The value λ_2 for the acids concerned (acetic, propionic, butyric) should be approximately identical, while the value of λ_1 increases with increase in mol. wt. (and b.p.) of the acid. This means that, in proportion to rise in mol. wt. affinity of acid for catalyst also increases. In the light of the above, the fact also becomes understandable of increased yields of methyl propionate and methyl butyrate (based on reacting acid) with rise in temperature.

SUMMARY

1. The theoretical possibility of the formation of esters by reaction of dimethyl and diethyl ethers with acids (acetic, propionic, butyric) in the gas phase has been experimentally established.

2. The most effective of the catalysts tested, ensuring high yields of ester, long life, and absence of secondary products, was phosphoric acid, with activated carbon (AR-3 brand) as carrier.

3. The optimum process conditions for obtaining methyl esters are a volume rate of flow of 0.5 liter/liter cat•hr. temperature 270°, and a dimethyl ether : acid ratio of 2 : 1 in the case of acetic, and of 4+7 : 1 for propionic and butyric acids. Under these conditions, the ester yields on acid used reached 93-94% for methyl acetate, 72% for methyl propionate, and 67% for methyl butyrate.

In the production of ethyl acetate optimum conditions are: temperature 180°, volume rate of flow 0.5 liter/liter cat•hr; whereby the yield of acetate reaches 90%.

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STUDY OF THE RADICAL REACTIONS OF PHOSPHORUS PENTAPHENYL

IV. REACTIONS OF PHOSPHORUS PENTAPHENYL WITH METHYL IODIDE. STUDY OF THE MECHANISM OF THE RADICAL REACTIONS OF PHOSPHORUS PENTAPHENYL WITH THE AID OF DIPHENYLPICRYLHYDRAZINE AND DIPHENYLPICRYLHYDRAZYL

G. A. Razuvaev, N. A. Osanova and I. A. Shlyapnikova

It was established earlier [1-3] that most of the phosphorus pentaphenyl reactions studied have a radical mechanism. Decomposition of phosphorus pentaphenyl proceeds with the breaking of one or two phenyl radicals. All reactions of phosphorus pentaphenyl with polyhalogen derivatives (chloroform, carbon tetrachloride, pentachloroethane) take place with the rupture of a phenyl radical. It was of interest to study the reaction of phosphorus pentaphenyl with alkyl monohalides. To this end the reaction with methyl iodide was investigated. It was possible to assume a molecular reaction with with formation of tetraphenylphosphonium iodide and toluene, according to the equation $(C_6H_5)_5P + CH_3I \rightarrow (C_6H_5)_4PI + C_6H_5CH_3$.

Actually, the reactions are much more complex, since it was possible to separate as the main products, tetraphenylphosphonium iodide, benzene, and iodobenzene; and as secondary products – toluene, diphenyl, methane and ethane.

Most of the phenyl radicals split off hydrogen from methyl iodide with formation of benzene. The other phenyl radicals split off iodine from methyl iodide, forming iodobenzene. It should be noted that in the reactions of phosphorus pentaphenyl with chloroform the phenyl radicals split off only hydrogen. Obviously, the phenyl radical splits hydrogen and iodine with about equal probability from methyl iodide. From consideration of the products obtained it is possible to suggest the following series of reactions:

$$(C_6H_5)_5P \rightarrow (C_6H_5)_4P \cdot + C_6H_5 \cdot$$

$$(C_6H_5)_4P \cdot + CH_3I \rightarrow (C_6H_5)_4PI + CH_3 \cdot$$

$$C_6H_5 \cdot + CH_3I \rightarrow C_6H_6 + (\cdot CH_2I)$$

$$C_6H_5 \cdot + CH_3I \rightarrow C_6H_5I + CH_3 \cdot$$

$$C_6H_5 \cdot + CH_3 \cdot \rightarrow C_6H_5CH_3$$

$$CH_3 \cdot + CH_3I \rightarrow CH_4 + (\cdot CH_2I)$$

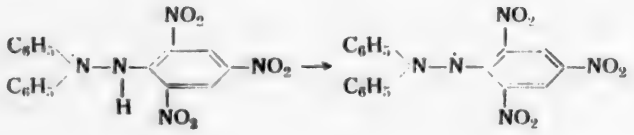
$$2CH_3 \cdot \rightarrow C_2H_6$$

$$2C_6H_5 \cdot \rightarrow C_6H_5{-}C_6H_5$$

and to suppose that the process has a free-radical mechanism.

In the earlier work, we used the method of radical fixation on mercury to show the radical mechanism of certain reactions of phosphorus pentaphenyl. A very real disadvantage of this method is the presence of a heterogeneous system.

At the present time for the study of radical reactions α,α'-diphenyl-β-trinitrophenylhydrazyl is used – a dark-violet colored radical, easily soluble in organic solvents; also, α,α'-diphenyl-β-trinitrophenylhydrazine which in reaction with free radicals easily loses hydrogen, and is thus converted into α,α'-diphenyl-β-trinitrophenyl-hydrazyl.



The orange-colored solution of diphenylpicrylhydrazine in the presence of free radicals assumes the violet color of diphenylpicrylhydrazyl. But if a radical reaction proceeds in the presence of diphenylpicrylhydrazyl then conversely, the color quickly changes from violet to orange.

The radical mechanism of the above-described reaction of phosphorus pentaphenyl with methyl iodide was confirmed by us in the manner indicated. We also checked the earlier work on phosphorus pentaphenyl reactions [3]. In carrying out reactions of decomposition of phosphorus pentaphenyl into benzene and pyridine in the presence of mercury, attachment of the phenyl radicals to mercury was not observed; but in reactions with diphenylpicrylhydrazine and diphenylpicrylhydrazyl, it was possible (in the case of benzene) to detect the presence of free radicals in solution, although with pyridine a negative result was obtained.

In all probability, in the given case, there is intramolecular breakdown (decomposition) of the phosphorus pentaphenyl. By this method, indeed, it was possible to confirm the presence of free radicals in the reaction of phosphorus pentaphenyl with alcohols and polyhalides, and their absence with acetic acid. The experimental results obtained are given in the Table.

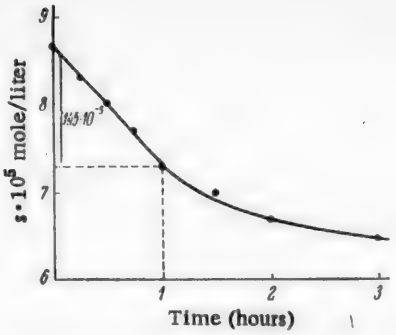
Solvent	Color of Solutions			
	I	II	III	IV
Benzene	Dark yellow	Darkens and remains dark red	Violet	Reddens
Pyridine	Orange	Unchanged	Dark red	Unchanged
Methanol	Dark yellow	Darkens and remains dark red	Violet	Reddens
Methyl iodide	Dark yellow	Darkens and remains dark red	Violet	Reddens
Chloroform	Yellow	Darkens and again becomes yellow	Violet	Becomes yellow
Acetic acid	Yellow	Unchanged	Violet, quickly to yellow	The same as in blank test

Remarks: I) Diphenylpicrylhydrazine in solvent (blank test); II) phosphorus pentaphenyl with solvent in the presence of diphenylpicrylhydrazine; III) diphenylpicrylhydrazyl in solvent (blank test); IV) phosphorus pentaphenyl with solvent in the presence of diphenylpicrylhydrazyl.

Study of the reaction mechanism of phosphorus pentaphenyl with chloroform was somewhat more detailed.

By means of the photocolorimetric method it was easily possible to follow timed changes in the concentration of the diphenylpicrylhydrazyl, and to make an approximate calculation of the number of free radicals emanating from the cell.

We carried out the reaction of phosphorus pentaphenyl with chloroform in the presence of diphenylpicrylhydrazyl at 20° and concentration of the phosphorus pentaphenyl of 1.8×10^{-3} mole/liter. Concentration of the diphenylpicrylhydrazyl in the selected tests was determined with the aid of the photonephecolorimeter FNK-51 (designed by the Physicotechnical Institute of the Gorky Univ.) From the experimental data the kinetic curve was constructed as shown:



Changes in concentration of diphenylpicrylhydrazyl in the reaction of phosphorus pentaphenyl with chloroform.

The graph shows that the decrease in concentration of the diphenylpicrylhydrazyl for 1 hour equalled 1.45×10^{-5} mole/liter, where, by simple calculation we have, in 1 ml of solution, the number of radicals freed from the cell (mol.) in one second as:

$$\frac{1.45 \cdot 10^{-5} \cdot 6.06 \cdot 10^{23}}{1000 \cdot 3600} \approx 2.4 \cdot 10^{18}.$$

EXPERIMENTAL

The Reaction of Phosphorus Pentaphenyl with Methyl Iodide

10 g of phosphorus pentaphenyl was heated with 44 g methyl iodide in a sealed tube for 20 hours at 90°. On opening the tube a sample of the gases that separated during reaction was withdrawn; analysis of which was effected with the aid of the volume chromathermographic gas analyzer of the GOKhT-3 type. Ethane was adsorbed on silica gel, methane on carbon. In 25 ml of gaseous mixture 0.9 ml/liter ethane and 6.2 ml methane were found. The solvent was distilled off; the residue was redistilled with water vapor, in which 0.19 g diphenyl with m.p. 68° was separated. A sample was mixed with pure diphenyl of m.p. 69°. The residual tetraphenylphosphonium iodide, after distillation with water vapor, was washed with ether, benzene, and recrystallized from hot water. 9.7 g (quantitatively) of tetraphenylphosphonium iodide of m.p. 315° was separated. The mixed m.p. with an iodide obtained in the known manner according to Dodonov [4] was 325°. From the solvent distilled off initially, the following fractions were separated: (1) 41.5-45.2°, (2) 45-78°, (3) 80-120°, (4) 150-200°. The first fraction was methyl iodide. From the second fraction, by repeated distillation, one of more limited b.p. range (60-78°) was recovered, in which, by nitration, benzene was identified; 0.55 g of m-dinitrobenzene with m.p. 86° was separated. The mixed melting point with pure m-dinitrobenzene was 89°. In the third fraction toluene was found; after oxidation of this fraction with potassium permanganate, 0.04 g benzoic acid of m.p. 118° was obtained. The mixed melting point with pure benzoic acid was 121°. The fourth fraction was iodobenzene (0.15 g) which was separated as phenyliodochloride by passing chlorine through a chloroform solution of this fraction. Decomposition temperature of the obtained phenyliodochloride was 107°; the mixed m.p. with a known sample was 110°. According to literature indications its decomposition temperature is 110-136° [5].

Synthesis of α,α'-Diphenyl-β-trinitrophenylhydrazyl [6]

0.6 g diphenylpicrylhydrazine was dissolved in 9 ml pure chloroform and shaken up with 7 g PbO_2 and 0.5 g calcined Na_2SO_4 for 1 hour. After a brief shaking, the violet diphenylpicrylhydrazyl formed. The solution was separated from the precipitate, the chloroform distilled off in vacuum, and the residue mixed with double its volume of ether. After several hours standing, violet prisms separated; these were washed with ether, and used in the experiments.

SUMMARY

1. Reactions of phosphorus pentaphenyl with methyl iodide proceed through a radical mechanism. As main products, tetraphenylphosphonium iodide, benzene, and iodobenzene were separated. By-products were diphenyl, toluene, methane, and ethane.

2. In studying the reactions of phosphorus pentaphenyl in the presence of diphenylpicrylhydrazine and diphenylpicrylhydrazyl we confirmed the ionic mechanism of the reaction with acetic acid and the presence of free radicals in reactions with benzene, methyl iodide, polyhalides, and alcohols. The breakdown into pyridine is probably intramolecular.

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CYCLOALKYLATION OF AROMATIC COMPOUNDS

XI. ON THE PRODUCT OF CONDENSATION OF CYCLOHEPTANOL WITH BENZENE

N. G. Sidorova and I. P. Tsukervanik

We have already studied the condensation of cycloheptanol (suberol) with benzene and concluded that the principal reaction product is cycloheptylbenzene [1]. Up to now, this hydrocarbon was not known. Our conclusions were questioned by Pines et al. [2]. These authors carried out the condensation of cycloheptanol and cycloheptene with benzene in the presence of various condensation agents, including aluminum chloride, and compared the products obtained with phenylcycloheptane synthesized by other methods. According to their results, the product of the reaction of cycloheptanol with benzene in the presence of aluminum chloride contains only 10% phenylcycloheptane.

However, the condensation conditions noted by these authors differed markedly from ours. In an attempt to reduce the various side-reactions (including isomerization) we carried out the condensation under relatively flexible conditions: namely, with a large excess of benzene at moderate temperature and with absence of any large excess of $AlCl_3$. Since too much $AlCl_3$ acts unfavorably, it is important to avoid even temporary excesses; thus sequence of reagent additions is of great significance. We accomplished the condensation as follows: finely ground $AlCl_3$ in small amounts was added to the solution of cycloheptanol in benzene with vigorous stirring. Each new addition of $AlCl_3$ was made only after nearly complete solution of the preceding amount. Then the mixture was heated over the water bath, the temperature of which was gradually raised in proportion as HCl slowly separated.

Pines et al. carried out the reaction under different conditions; they added the cycloheptanol to the whole of the $AlCl_3$ in benzene. With such a method of adding the reagents there was turbulent reaction accompanied by frothing of the mixture.

It was, naturally, to be expected that reactions undertaken under such different conditions could result in different products. Therefore, we again made a study of the condensation of cycloheptanol with benzene. Now, having had experience in performing such condensations without isomerization [3], we undertook the reaction under still more flexible (mild) conditions: at a lower temperature, with less (0.7 g equiv.) $AlCl_3$, and a still larger excess of benzene. Moreover, in order to moderate the effect of $AlCl_3$, water was added to the reaction mixture, and for removing HCl at the lowest possible temperature it was drawn off by pump. The product (73%) obtained by us under these conditions, from its b.p. and smell, differed appreciably from the isomeric methylphenylcyclohexanes. It consisted mainly of phenylcycloheptane. From this were obtained, with good yields, crystalline derivatives, of which the m.p. corresponded to the literature data for phenylcycloheptane derivatives [2, 4]. It was thus shown that it is possible to achieve the reaction of cycloheptanol with benzene in the presence of $AlCl_3$ without appreciable isomerization.

Apparently the seven-membered rings are more stable than is usually supposed. Therefore, although cycloheptane and its homologs – as M. B. Turova-Polyak [5] has shown – in the presence of $AlCl_3$ is readily converted into cyclohexane hydrocarbons, yet in some Friedel-Craft reactions the seven-membered rings are easily formed and remain unchanged. Several reactions are known of ring-closing with formation of benzosuberane derivatives [6].

By way of comparison we performed a condensation with inverse sequence of reagent addition, and obtained a small yield (35%) of a product boiling within a wide range and markedly differing from that obtained by us under flexible (mild) conditions.

EXPERIMENTAL

Synthesis of cycloheptanol (suberol). By the action of nitrosomethylurethan on cyclohexanol, suberone was obtained with a yield of 45-50% of theoretical. B.p. 172-175° (731 mm), n_D^{20} 1.4607. Semicarbazone with m.p. 162°.

The suberone was hydrogenated in a rotary autoclave in alcoholic solution over Raney nickel (15%) at 120° and 65 atm. hydrogen pressure measured at 15°. On completion of the reaction the contents of the autoclave were filtered and column-distilled. Yield of suberol 90%.

B.p. 178-180° (735 mm), n_D^{17} 1.4747. Negative reaction for the carbonyl group. Literature data for suberol, b.p. 180-187, n_D^{20} 1.4760 [2].

Condensation of Suberol with Benzene

Reactions under flexible (mild) conditions. Five drops of water were added to 8.0 g (0.07 mole) of suberol and 180 ml (2 mole) of benzene, and gradually, in small portions with intermittent shaking, 6.7 g (0.05 mole) of finely ground commercial $AlCl_3$ was added. The addition lasted 2 hours. The mixture was left for 5 days; periodically, HCl was withdrawn by means of a water-jet pump through the upper end of the condenser. When separation of HCl became vigorous two or three drops of water were added to the reaction mixture. Such addition was repeated three times. Within five days and even with pumping, the evolution of HCl had nearly ceased (litmus test). The reaction was completed by heating first at 40-55° for 3-4 hours and then at 70-80° for a few minutes. The mixture was broken down with dilute hydrochloric acid, washed with water, dried over $CaCl_2$, and analyzed. 8.9 g (73%) of product was obtained:

B.p. 148-150° (37 mm), 135-136.5° (18 mm), d_4^{20} 0.9478, n_D^{20} 1.5286, MR_D 56.63; calc. 56.43.

Acetamino derivative – small tablets of m.p. 172.5-173.5 (from dilute alcohol).

Found %: N 6.58. $C_{15}H_{21}ON$. Calculated %: N 6.06.

Diacetamino derivative – thin lustrous plates of m.p. 239-240° (from dilute alcohol); separated from the filtrate after removal of the mono-acetamino derivative.

Benzamino derivative – with rapid cooling of the alcoholic solution precipitated as small plates or flakes which, in solution, gradually change into acicular forms of m.p. 173.5-174.5°.

Found %: N 5.12. $C_{20}H_{23}ON$. Calculated %: N 4.78.

Sulfamide – small plates or flakes of m.p. 142-143° (from dilute alcohol).

Found %: N 5.22. $C_{13}H_{19}SO_2N$. Calculated %: N 5.53.

These derivatives could be easily and thoroughly purified. Apparently, admixtures therewith were only di-substituted derivatives.

The reaction under more rigid conditions was effected as described in the article of Pines et al. [2]. A solution of 8.5 g (0.075 mole) suberol in 25 ml benzene was added to 50 ml benzene and 10 g (0.075 mole) $AlCl_3$ with stirring during 30 minutes. When a great part of the solution was added, sudden and vigorous reaction began with intensive separation of HCl and formation of insoluble resins. After adding the whole of the suberol the reaction mixture was heated on the water bath to boiling point for 2 hours. Further procedure was as usual. 4.7 g (35%) of a fraction was obtained with b.p. of 115-124° (12 mm). With repeated distillation over sodium a product separated with:

B.p. 124-127° (18 mm), d_4^{20} 0.9460, n_D^{20} 1.5224, MR_D 56.18; calc. 56.43.

From its smell the substance differed markedly from the product of the preceding condensation.

SUMMARY

By condensation of cycloheptanol with benzene in the presence of aluminum chloride cycloheptylbenzene (yield 73%) of theoretical) was obtained.

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CYCLOALKYLATION OF AROMATIC COMPOUNDS

XII. SYNTHESIS AND SOME CONVERSIONS OF 1-METHYL-2-PHENYL- AND 1-METHYL-3-PHENYLCYCLOHEXANES

N. G. Sidorova

In view of the considerable difficulties that arise in identifying the condensation products of methylcyclohexanols with benzene, we synthesized two of the possible reaction products: 1-methyl-2-phenyl- and 1-methyl-3-phenylcyclohexanes (as mixtures of the cis- and trans- forms) for comparison therewith of hydrocarbons obtained by alkylation.

1-Methyl-2-phenylcyclohexane was prepared by us jointly with I. P. Tsukervanik in some of our previous work [1]; but neither the hydrocarbons nor the derivatives obtained for identification were sufficiently purified. This hydrocarbon and 1-methyl-3-phenylcyclohexane were recently synthesized by Linsk [2] and identified by production of the dinitrophenyl hydrazones of the acetyl derivatives. Kursanov [3] has described as 1-methyl-3-phenylcyclohexane the alkylation product of benzene with 1-chloro-3-methylcyclohexane in the presence of aluminum chloride. Evidently, the substance he obtained was a mixture of isomeric methylphenylcyclohexanes. Braun [4] obtained 1-methyl-3-phenylcyclohexane by condensing 3-methylcyclohexane with aniline in the presence of HCl, hydrogenating the product, and separating the amino groups.

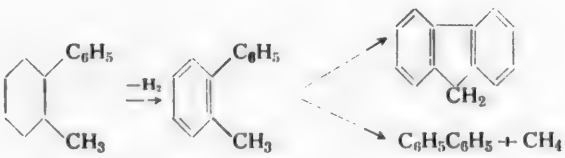
We performed the synthesis in the usual way [5] from the corresponding methylcyclohexanones via tertiary alcohols and cycloolefins, and obtained isomeric methylphenylcyclohexanes as a mixture of stereoisomers.

The latter stage of the synthesis – hydrogenation in the presence of Raney nickel – proceeded at different rates for both isomers. In accordance with Lebedev's rule [6] 1-methyl-2-phenylcyclohexene was hydrogenated with appreciable speed at a temperature not lower than 120-125°, whereas the 1,3-isomer quickly combined hydrogen even at 80°.

The benzamino derivatives obtained from 1-methyl-2-phenyl- and 1-methyl-3-phenylcyclohexanes, on crystallizing from alcohol, separated as crystals in two forms – small, lusterless needles agglomerating into balls, and transparent flakes. In both cases the matte crystals had the higher m.p.

We studied the hydrogenation and dehydrogenation of 1,2- and 1,3-methylphenylcyclohexanes. By hydrogenation mixtures of the corresponding stereoisomeric methylcyclohexylcyclohexanes were obtained.

1-Methyl-2-phenylcyclohexane was dehydrogenated over platinized carbon at 350-370°. Fluorene was obtained as the principal product. Moreover, a small amount of liquid fractions and traces of diphenyl separated out. Therefore, under these conditions we have a partial cleavage of the methyl group from the tertiary carbon atom



Cases of the splitting off of nonangular alkyl groups are known in the literature [7].

In the dehydrogenation of 1-methyl-2-phenylcyclohexane with selenium at 380° only fluorene was obtained. Dehydrogenation of 1-methyl-3-phenylcyclohexane over platinized carbon at 300-310° gave m-methyldiphenyl.

EXPERIMENTAL

Synthesis of 1-Methyl-2-phenylcyclohexane

2-Methylcyclohexanol was obtained by hydrogenation of o-cresol with Raney nickel at 180° and 100 atm. hydrogen pressure.

2-Methylcyclohexanone was obtained by oxidation of 2-methylcyclohexanol with sodium bichromate [5] with subsequent steam distillation of the reaction mixture. Yield 80-85%. B.p. 162-163° (728 mm).

1-Phenyl-2-methylcyclohexanol [8] was obtained by the Grignard reaction from equimolecular amounts of bromo-benzene, magnesium, and 2-methylcyclohexanone in absolute ether. The ketone addition was ice-cooled. After decomposing with ammonium chloride solution the ether layer was separated, dried with potash, and fractionated. Yield 80%, b.p. 105-108° (2 mm) n_D^{20} 1.5366.

1-Methyl-2-phenylcyclohexene. The alcohol was dehydrated by passing over aluminum oxide heated to 320-330° (layer of 25 cm length). The reaction product was dried with calcium chloride and distilled over sodium. B. p. 135° (28 mm), n_D^{20} 1.5580. In some of the experiments unpurified alcohol was dehydrated, from which only the unreacting initial substances were distilled. In such cases the yield of olefin was 66% (reckoned on the initial ketone).

1-Methyl-2-phenylcyclohexane. 1-Methyl-2-phenylcyclohexene was hydrogenated in a rotary autoclave in alcoholic solution over Raney nickel (10% of weight of hydrocarbon) at 120-125° and 55 atm hydrogen pressure (at 15°). The reaction was completed after absorption of a calculated amount of hydrogen. The end of the reaction could be observed through a sharp change in the rate of hydrogenation. The contents of the autoclave were filtered through a dense glass filter with a layer of asbestos in the distillation retort, and fractionated. The residue, after driving off the alcohol, was redistilled over sodium.

B.p. 133-143° (36 mm), n_D^{20} 1.5244, d_4^{20} 0.9465, MR_D 56.33; calc. 56.43.
Found %: C 89.42; H 10.19. $C_{13}H_{18}$. Calculated %: C 89.59; H 10.41.

Literature data for 1-methyl-2-phenylcyclohexane: b.p. 62-63° (0.4 mm), n_D^{20} 1.5285 [2].

Benzamino derivative. The hydrocarbon was nitrated in the usual way and the nitro-compound reduced with tin and hydrochloric acid. On completion of the reaction the unreacted hydrocarbon and traces of nitro-compound were distilled off with steam. Excess alkali was added to the residue and the amine distilled with water vapor. It was recovered from the distillate with benzene, dried with caustic potash, and again distilled. B.p. 182-185° (25 mm), n_D^{20} 1.5622, d_4^{20} 1.0144. The amine was benzoylated in the usual way. On crystallization of the benzamino derivative from alcohol, two kinds of crystals formed. These were sorted out and separately recrystallized. Two benzamino derivatives were thus obtained. One of these (transparent flakes) had m.p. 196-197°.

Found %: N 4.87. $C_{20}H_{23}ON$. Calculated %: N 4.78.

The second benzamino derivative was in the form of matte balls of m.p. 201-202°.

Found %: 5.01. $C_{20}H_{23}ON$. Calculated %: N 4.78.

1-Methyl-2-phenylcyclohexane was hydrogenated in an alcoholic medium in the presence of freshly prepared Raney nickel (10% of weight of hydrocarbon) at 180-190° and 55 atm hydrogen pressure at 15°. Mixing was continued until complete cessation of the hydrogen absorption. The reaction mixture was filtered in a distillation flask, and after the alcohol was distilled off the mixture of stereoisomeric 1-methyl-2-cyclohexylcyclohexanes was distilled over sodium. Yield 96%.

B.p. 141-142° (39 mm), n_D^{20} 1.4800, d_4^{20} 0.8915, MR_D 57.41; calc. 57.83. Aniline pt. 50.0°.
Found %: C 86.34; H 13.39. $C_{13}H_{24}$. Calculated %: C 86.59; H 13.41.

Dehydrogenation of 1-methyl-2-phenylcyclohexane with selenium [9]. A mixture of 2.5 g hydrocarbon and 3.4 g selenium was heated to boiling in a long refractory test tube. The hydrogen selenide that separated was absorbed in alkaline solution. As dehydrogenation proceeded, the boiling point of the mixture rose and reached 300°. Heating was continued for 90 hours, and within that time dehydrogenation was not complete. A product was obtained having b.p. 118-120° (11 mm) and n_D^{20} 1.5632.

Further dehydrogenation of this material with selenium was continued in a sealed tube at 350-380° for 15 hours. After cooling, the contents of the tube were crystallized. The crystals were of fluorene which after treatment with active carbon and recrystallization from alcohol had m.p. 114-115°. A check of the mixture with a known sample of fluorene showed no depression of melting point.

Dehydrogenation with platinum [10]. 9.2 g of 1-methyl-2-phenylcyclohexane was passed for 2.5 hours together with a weak current of hydrogen through a tube filled to the extent of 30 cm with activated carbon and 50 cm with platinized carbon (20% platinum) and heated to 350-370° (within a short time the temperature rose to 400°). The calalyzate in the receiver was quickly crystallized. On distillation, about 0.5 ml of liquid was distilled off: b.p. 103-105° (5 mm) and n_D^{20} 1.5830. When cooled in a freezing mixture, some crystals were deposited, which, after recrystallizing from alcohol, had m.p. of 72°, and, mixed with diphenyl of m.p. 70°, still melted at 72°. Evidently, these crystals are diphenyl mixed with fluorene. The liquid part of the product is a mixture of the original substance with the products of dehydrogenation. The residue, after distillation, was pure fluorene of m.p. 114-115°. Yield 6.2 g.

Synthesis of 1-Methyl-3-phenylcyclohexane

The synthesis of 1-methyl-3-phenylcyclohexane was in all respects similar to that of 1-methyl-2-phenylcyclohexane. As initial material 3-methylcyclohexanol was used, from which 3-methylcyclohexanone was obtained with a yield of 90%. B.p. 166-168° (727 mm). Yield of 3-methyl-1-phenylcyclohexene was 55%, reckoned on the ketone. B.p. 141-143° (25 mm), n_D^{20} 1.5586.

1-Methyl-3-phenylcyclohexane. 10 g of the hydrocarbon was fed into the autoclave, together with 1.5 g of freshly prepared Raney nickel, 15 ml ethyl alcohol, and hydrogen compressed to 60 atm (20°). Stirring and heating of the autoclave proceeded simultaneously. At 80° hydrogen absorption was sufficiently vigorous, so that the temperature was not raised higher. Stirring was continued until hydrogen absorption ceased. The contents of the autoclave were filtered and fractionated. 8.2 g of 1-methyl-3-phenylcyclohexane.

B.p. 133-134° (26 mm), n_D^{20} 1.5286, d_4^{20} 0.9464, MR_D 56.71; calc. 56.43.
Found %: C 89.29; H 10.41. $C_{13}H_{18}$. Calculated %: C 89.59; H 10.41.

Literature data for 1-methyl-3-phenylcyclohexane: b.p. 78-79° (1.3 mm), n_D^{20} 1.5232 [2].

The benzamino derivative was obtained in the same way as that of 1-methyl-2-phenylcyclohexane, but without separation of the amine in a pure state. With slow crystallization from alcohol bright, lustrous, quadrangular flakes and dull-surface small balls were formed. The crystals were stored out and separately recrystallized. The flake-like crystals melted at 167-168°.

Found %: N 5.19. $C_{20}H_{23}OH$. Calculated %: N 4.78.

The matte crystals, after purification were fine needle-like forms, agglomerating into balls. M.p. 174-175°.

Found %: N 4.59, 5.25. $C_{20}H_{23}ON$. Calculated %. N 4.78.

In addition to these two forms, a small amount of still another benzamino derivative was obtained by crystallization: lustrous needles of m.p. 155-156°. This evidently was the o-isomer.

Found %: N 4.58. $C_{20}H_{23}ON$. Calculated %: N 4.78.

1-Methyl-3-phenylcyclohexane was hydrogenated in alcoholic solution in the presence of Raney nickel (15%) at 180-190° and a hydrogen pressure of 115 atm (at 25°). Stirring was continued until complete cessation of hydrogen absorption. From 10 g of 1-methyl-3-phenylcyclohexane 8.1 g of 1-methyl-3-cyclohexylcyclohexane was obtained (mixture of stereoisomers).

B.p. 123-124° (20 mm), n_D^{20} 1.4859, d_4^{20} 0.8930, MR_D 57.92; calc. 57.83. Aniline point 38.0°. Found %: C 86.27; H 13.69. $C_{13}H_{24}$. Calculated %: C 86.59; H 13.41.

Dehydrogenation of 1-methyl-3-phenylcyclohexane. 7.0 g of 1-methyl-3-phenylcyclohexane was passed for 3 hours in a weak hydrogen current through a reaction tube filled with platinized carbon (20%) at 300-310°. The catalyzate obtained (4.7 g) was distilled over sodium and divided into two fractions: (1) b.p. 139-153° (25 mm), n_D^{20} 1.5671, 3.0 g. (2) b.p. 153-155° (25 mm), n_D^{20} 1.6012, d_4^{20} 1.0135, MR_D 56.83; calc. 55.03; EMR_D 1.80.

The second fraction was pure m-methyldiphenyl. Oxidation with a 2% solution of $KMnO_4$ [11] yielded pure m-phenylbenzoic acid of m.p. 168°, crystallizing from 50% alcohol into large quadrangular flakes. By nitrating the m-methyldiphenyl, we obtained 4,4'-dinitro-3-methyldiphenyl having m.p. 196° [12].

SUMMARY

1. 1-Methyl-2-phenyl- and 1-methyl-3-phenylcyclohexane were synthesized in the mixed cis- and trans- forms.

2. By hydrogenation of these hydrocarbons, mixtures of the stereoisomeric 1-methyl-2-cyclohexyl- and 1-methyl-3-cyclohexylcyclohexanes were obtained.

3. Dehydrogenation of 1-methyl-2-phenylcyclohexane with selenium yielded fluorene; dehydrogenation over platinized carbon at 350-370° gave fluorene with traces of diphenyl. On dehydrogenating 1-methyl-3-phenylcyclohexane over platinized carbon at 300-310° m-methyldiphenyl was obtained.

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SILICOORGANIC DERIVATIVES OF BORIC ACID – TRIS(TRIALKYLSILYL) BORATES AND POLYBORAORGANOSILOXANES

M. G. Voronkov and V. N. Zgonnik

Up to now, silicoorganic esters of boric acid have been hardly noticed in literature, although there are some indications as to the possibility of producing them.

Thus, according to patent references [1], on boiling trimethylethoxysilane or other trimethylalkoxysilanes with boric acid in the presence of n-toluenesulfonic acid, tris(trimethylsilyl) borate (b.p. 90°) is formed [1]. But the b.p. mentioned is extremely low, and could not positively correspond to $[(CH_3)_3SiO]_3B$ since its carbon analog $[(CH_3)_3CO]_3B$ has a b.p. of 175° [2].

In other patents [3], it is stated that tris(trimethylsilyl) borate is a catalyst of the condensation reaction R_nSHCl_{3-n} (n = 0–2) with aromatic hydrocarbons.

In contrast to patent [1], there are also statements to the effect that the reaction of alkoxysilanes with boric acid proceeds differently, with formation of alkyl borates [4,5] e.g., according to the equation

$$3Si(OR)_4 + 5B(OH)_3 \rightarrow 4B(OR)_3 + 3Si(OH)_4$$

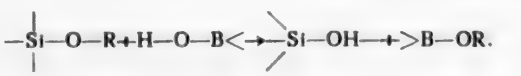
Attempts to obtain bis(triethylsilane)phenyl borate $C_6H_5B[OSi(C_2H_5)_3]_2$ by reaction of triethylbromosilane with phenylboric acid met with little success [6]; as was the case with our attempt to obtain tris(triethylsilane) borate by the action of BBr_3 on triethylsilanol [7]. * By substituting triethylsilanol for its sodium derivative in the reaction with BBr_3 tris(triethylsilane)borate $[(C_2H_5)_3SiO]_3B$ is formed [7]. But neither its yield, its boiling point and other physical constants, or analytical data are provided.

Besides this extremely meager information, there is one original work [11] and a whole series of patents [5, 12-25] describing either the methods of obtaining and the properties of high-molecular silicoorganic compounds containing boron [12-17] – and especially such substances as "bouncing putty" [18-20] – or the use of boron compounds for the preparation of silicoorganic polymers [21-25].

The purpose of the present work is to develop methods for the synthesis of silicoorganic esters of orthoboric acid, tris(trialkylsilane) borates, $(R_3SiO)_3B$, and also polyborasiloxanes with a framework of alternating atoms of silicon, oxygen, and boron.

The attempts made by us to obtain tris(trimethylsilyl) borate in accord with patent directions [1], by heating boric acid with trimethylethoxysilane and also with trimethylmethoxysilane, in all cases proved unsuccessful. In not one of the tests undertaken under various conditions, both in the presence of catalysts and without, was the formation of $[(CH_3)_3SiO]_3B$ to any practical degree observable (maximum yield 3-5%) and the reaction products turned out to be triethyl borate and hexamethyldisiloxane.

Thus, it was possible to conclude (this is confirmed also by statements of other authors [4, 5]), that boric acids react with alkoxysilanes with formation of alkyl borates, in accord with the scheme:



* Also mentioned in the literature is the reaction of boron halides with siloxanes [3, 8, 9] and alkoxysilanes leading to the formation of the corresponding halosilanes.

TABLE 1

Tris(trialkylsilyl) Borates

$(R_3SiO)_3B$	B.p. (mm)	d_4^{20}	n_D^{20}	% B		% Si		Method of production	Yield (%)
				Found	Calc.	Found	Calc.		
$[(CH_3)_3SiO]_3B$	184.5° (776)	0.8285	1.3860	3.86; 3.76	3.89	29.7; 29.4	30.27	$(CH_3)_6Si_2O + B_2O_3$	26
$[(CH_3)_3SiO]_2B$	48 (5)	0.8299	1.3859	3.88; 3.87	3.89	30.9; 29.6	30.27	$(CH_3)_3SiCl + B(OH)_3$	26.5
$CH_3[(C_2H_5)_2SiO]_3B$	131—133 (5)	0.8751	1.4225	2.99; 3.00	2.99	23.2%; 23.36	23.24	$CH_3(C_2H_5)_2SiOCH_3 + B(OH)_3$	73
$[(C_2H_5)_3SiO]_3B$	310—312 (780)	0.8918	1.4379	2.65; 2.65	2.67	20.82; 20.90	20.83	$(C_2H_5)_3SiOCH_3 + B(OH)_3$	94
$[(C_2H_5)_3SiO]_2B$	178—179 (13)		1.4382	2.76; 2.79	2.67	21.5; 22.0	20.83	$(C_2H_5)_3SiCl + B(OH)_3$	24.5
$[CH_3(n.-C_3H_7)_2SiO]_3B$	157—160 (1)	0.8668	1.4332	2.38; 2.44	2.42	18.6; 19.2	18.86	$CH_3(C_3H_7)_2SiOCH_3 + B(OH)_3$	74

From this starting point we attempted to use the reaction as set forth above for the synthesis of trialkyl borates from tetraalkoxysilanes and boric acid. But it was found that, in distilling the silicoethyl ester over boric acid (molar ratio 3 : 4) there was preferentially formed not the triethyl borate but ethyl alcohol, and this with high yield. The reaction proceeds as follows

$$3Si(OC_2H_5)_4 + 4B(OH)_3 \rightarrow 12C_2H_5OH + 3SiO_2 \cdot 2B_2O_3$$

Boric anhydride, on the other hand, reacts smoothly enough with tetraalkoxysilanes:

$$2B_2O_3 + 3Si(OR)_4 \rightarrow 4B(OR)_3 + 3SiO_2$$

This reaction is a convenient method for the synthesis of trialkyl borates, especially $B(OCH_3)_3$ and $B(OC_2H_5)_3$ that are the most difficult to accomplish, owing to the fact that they form azeotropic mixtures with the corresponding alcohols. The yield of trimethyl borate obtained by us in this way was about 60% of theoretical.

The formation of alcohols in the reaction of tetraalkoxysilane with boric acid showed that the reaction of alkoxysilanes with boric acids is really possible in accord with another general scheme

And actually it was found that, in reacting the high trialkylalkoxysilanes R_3SiOR' (preferably R_3SiOCH_3) with boric acid tris(trialkylsilyl) borates $(R_3SiO)_3B$ are formed, with yields above 70% of theoretical.

With the aid of this reaction, smoothly proceeding in the absence of any catalyst, according to scheme:

$$3R_3SiOR' + B(OH)_3 \rightarrow (R_3SiO)_3B + 3R'OH$$

we synthesized three silicoorganic esters of orthoboric acid, as shown in Table 1. However, we were unable to synthesize the tris(trimethylsilyl) borated in this way with any really satisfactory yield.

Tris(trimethylsilyl) borate was nevertheless obtained by us with a yield of 20% in another way, namely: reaction of hexamethyldisiloxane with B_2O_3 (at 350°), similar to that suggested earlier by us [26] for synthesizing tris(trialkylsilyl)phosphates $(R_3SiO)_3PO$. It should be pointed out that, unlike P_2O_5, B_2O_3 hardly reacts at all with hexaalkyldisiloxanes at temperatures below 250-230°. But at higher temperatures and preferably under pressure (in an autoclave) the reaction proceeds with formation of tris(trialkylsilyl) borates $3R_3SiOSiR_3 + B_2O_3 \rightarrow 2B(OSiR_3)_3$.

We have shown, moreover, that tris(trimethylsilyl) borates may be most easily and simply obtained (but with low yield) by heating trialkylchlorosilanes (but not bromosilanes [6]) with boric acid until cessation of hydrogen chloride evolution in accordance with the equation:

$$3R_3SiCl + B(OH)_3 \rightarrow (R_3SiO_3)B + 3HCl$$

In this way we obtained tris(trimethylsilyl)- and tris(triethylsilyl)-borates with yields of 26.5% and 24.5%, respectively.

Finally we have also found that tris(trialkylsilyl) borates may be obtained by reacting boric acid esters with trialkylsilanols in the presence of their sodium derivatives, as follows:

$$B(OR)_3 + 3R'_3SiOH \xrightarrow{R_3SiONa} 3ROH + (R'_3SiO)_3B$$

or with trialkylchlorsilanes in the presence of anhydrous $FeCl_3$

$$B(OR)_3 + 3R'_3SiCl \xrightarrow{FeCl_3} 3RCl + B(OSiR'_3)_3$$

In the latter case ferric chloride, acting as catalyst, brings about also the decomposition of $B(OSiR_3)_3$ as in equation

$$2B(OSiR_3)_3 \xrightarrow{FeCl_3} B_2O_3 + 2R_3SiOSiR_3$$

Therefore the reaction of trialkyl borates with trialkylchlorosilanes should be done with a minimum amount of ferric chloride which it is desirable to couple or decompose after distilling off the alkyl halide. The yields, of tris(triethylsilyl) borate in synthesis from tri-n-butyl borate and triethylsilanol or triethylchlorosilane (without removal of $FeCl_3$) are, respectively, 23.5 and 10%.

Tris(trialkylsilyl) borates are colorless liquids easily soluble in organic solvents, having the faint odor of trialkylsilanes. They are not soluble in water but are hydrolyzed very readily by aqueous solutions of alkali or weak acid. The higher esters hydrolyze more difficultly than the lower. They burn with a green flame, forming white vapor. The physical constants, yields, and analytical data of the tris(trialkylsilyl) borates obtained by us are given in Table 1.

The above-described methods of synthesizing tris(trialkylsilyl) borates were also used for obtaining polyborasiloxanes* of different structure. Thus, for example, by reacting boric acid with dimethyldiethoxysilane in the molar ratio of 1 : 3 a viscous, soluble polymer was obtained, having a boron content of 4.2%. The reaction proceeds easily, with formation of ethyl alcohol and also triethyl borates, and may apparently be represented as follows:

$$3nB(OH)_3 + 6n(CH_3)_2Si(OC_2H_5)_2 \rightarrow$$
$$\rightarrow [B_2O_3 \cdot 6(CH_3)_2SiO]_n + 9nC_2H_5OH + nB(OC_2H_5)_3.$$

The series of polyboraorganosiloxanes, the properties of which are here investigated, were obtained by us in reacting dimethyldiethoxysilane with boric acid in different ratios, and also by reacting the latter with diethyldimethoxysilane.

The reaction of boric acid with an equimolecular amount of methyltriethoxysilane proceeds with separation of approximately theoretical amounts of ethyl alcohol. A solid, insoluble, nonvolatile polymer is thereby formed, containing 5.3%B and corresponding to the formula: $B_2O_3 \cdot 4CH_3SiO_{1.5}$.

* Names in accord with the "oxa-aza" – nomenclature. The prefix "bora" indicates the replacement of Si atoms in the siloxane chain by B.

By changing the ratio of boric acid and alkylalkoxysilanes and also the structure of the latter, it is possible to obtain polyborasiloxanes with the specified content of boron distinguished by different properties. By reacting H_3BO_3 with $(C_2H_5)_2Si(OCH_3)_2$ and $(CH_3)_2Si(OC_2H_5)_2$ we obtained a series of polymers of this type, the properties of which we are studying.

Another convenient method of synthesizing polyborate organosiloxanes is the reaction of boric acid with alkylchlorosilanes R_nSiCl_{4-n} (n = 1-2). Thus, for example, in reacting dimethyldichlorosilane with $B(OH)_3$ in a molar ratio of 3 : 2, we obtained the polymer approximating in composition $[B_2O_3 \times 3(CH_3)_2SiO]_n$ and having the properties of "bouncing putty." The reaction proceeds according to the equation:

$$2B(OH)_3 + 3(CH_3)_2SiCl_2 \rightarrow 6HCl + [B_2O_3 \cdot 3(CH_3)_2SiO]_n.$$

The polyboraorganosiloxanes are liquids of varying degrees of viscosity, and also soluble or insoluble, flaky or coarse, solid substances. They, as also the tris(trialkylsilyl) borates, remain practically unchanged when heated to 300-350°, and are hydrolyzed with cleavage of the bond Si—O—B, forming boric acid more readily with increasing amounts of boron.

In conclusion we may remark that most of the proposed methods of synthesizing the trialkylsilyl esters of boric acid and the polyborasiloxanes are applicable also for obtaining the corresponding silicoorganic derivatives of other elements, and especially those of phosphorus. Our subsequent communications will be devoted to the latter.

EXPERIMENTAL

Initial reactions – Trialkylmethoxysilanes (except $(CH_3)_3SiOCH_3$) are obtained by reacting the corresponding trialkylsilanes with methyl alcohol in the presence of sodium methylate [27] or $ZnCl_2$. The trialkylsilanes, in turn, are prepared by the Grignard reaction from CH_3SiHCl_2 or $C_2H_5SiHCl_2$ and the corresponding hexaalkyldisiloxanes over $AlCl_3$ [28]. Triethylsilanol was produced by the method that we developed for synthesizing the heavy trialkylsilanols R_3SiOD, by washing triethylmethoxylsilane with water in a dioxane medium. Silicomethyl- and silicoethyl esters are commercial preparations. All the initial silicoorganic compounds were purified by column distillation. Their physical properties are given in Table 2.

TABLE 2

Properties of the Initial Silicoorganic Compounds

Formula	B.p.	n_D^{20}	Yield (%)
$(CH_3)_3SiOCH_3$	57°	1.3679	40
$CH_3(C_2H_5)_2SiOCH_3$ *	114	1.4000	24
$(C_2H_5)_3SiOCH_3$	141	1.4130	80
$CH_3(C_3H_7)_2SiOCH_3$ *	154.5	1.4125	92
$(C_2H_5)_2Si(OCH_3)_2$	134	1.4000	70
$(CH_3)_3Si(OC_2H_5)$	75	1.3742	42
$(CH_3)_2Si(OC_2H_5)_2$	114	1.3810	65
$CH_3Si(OC_2H_5)_3$	141	1.3832	—
$Si(OC_2H_5)_4$	168	1.3830	—
$Si(OCH_3)_4$	121	1.3689	—
$(C_2H_5)_3SiOH$	157	1.4330	75
$(CH_3)_3SiCl$	58	1.3885	82
$(C_2H_5)_3SiCl$	146	1.4313	90
$CH_3(C_2H_5)_2SiH$	78	1.3981	51
$(C_2H_5)_3SiH$	108	1.4120	75
$CH_3(n\text{-}C_3H_7)_2SiH$	127	1.4132	68
$(CH_3)_3SiOSi(CH_3)_3$	100	1.3774	—
$(C_2H_5)_3SiOSi(C_2H_5)_3$	236	1.4340	—

Tributyl borate was obtained by boiling 185.5 g (3 moles) of boric acid with 741 g (10 moles) butyl alcohol in a flask fitted with a reflux condenser and water trap until cessation of water separation. Subsequent distillation in vacuum gave 586 g (85%) of tributyl borate of b.p. 79° (1 mm), n_D^{20} 1.4087.

Boric acid and anhydride are commercially pure preparations. The former was ground into fine powder and held in a dryer over $CaCl_2$.

Analysis: The boron in tris(trialkylsilyl) borates and polyborasiloxanes was determined as boric acid by titrating a weighed amount of substance in aqueous dioxane or aqueous alcohol media in the presence of mannite with a 0.2 N NaOH solution (with thymol blue as indicator). The alkaline solution was titrated with aqueous dioxane or, correspondingly, with aqueous alcohol solution of pure boric acid of similar concentration, in which previously the B_2O_3 content had been gravimetrically determined.

The silicon content was found by difference from the sum of silicon and boron oxides formed by mineralizing a known weight of substance with a mixture of oleum and nitric acid, followed by roasting the oxides at 900°.

The synthesis of tris(triethylsilyl) borate. 52.7 g (0.36 mole) of triethylmethoxysilane and 6.2 g (0.1 mole) of boric acid were heated to boiling point for 6 hours. At the end of this time the b.p. of the reaction mixture fell from 141 to 78°. With subsequent distillation at 65-70° 8.7 g methyl alcohol (91%) passed over, with 9.8 g of unchanged triethylmethoxysilane, and 38.0 g of tris(triethylsilyl) borate of b.p. 139-143° (2 mm). Yield 94% of theoretical. After being twice distilled, it had b.p. 310-312° (780 mm) with constants as shown in Table 1. By direct distillation of triethylmethoxysilane over H_3BO_3 (without preliminary heating) the yield of tris(triethylsilyl) borate was 70%.

In a similar way $[CH_3(C_2H_5)_2SiO]_3B$ and $[(CH_3)_n\text{-}(C_3H_7)_2SiO]_3B$ were obtained with yields of 73% and 74% respectively.

Synthesis of tris(trimethylsilyl) borate from hexamethyldisiloxane and B_2O_3. 151.0 g (0.93 mole) of hexamethyldisiloxane and 41.8 g (0.6 mole) boric anhydride were heated in a steel autoclave of 0.25 liter capacity for 27 hours at 350°. On distillation of the liquid reaction products combined with an ether extract of unreacted excess B_2O_3, 50 g of unchanged hexamethyldisiloxane and 23 g of tris(trimethylsilyl) borate with b.p. of 175-185° were obtained, i.e., 20% of theoretical calculated on the reacted hexamethyldisiloxane. After a second distillation, the borate had the constants given in Table 1.

Synthesis of tris(trimethylsilyl) borate from $(CH_3)_3SiCl$ and H_3BO_3. 92.5 g (0.85 mole) of trimethylchlorosilane and 17.3 g (0.28 mole) of boric acid were heated to boiling for 15 hours until separation of hydrogen chloride had completely stopped. By fractional distillation of the reaction mixture 20.6 g (26.5%) of the crude tris(trimethylsilyl) borate was obtained with b.p. of 166-186°; the second distillation of which gave 12.8 g of the pure substance, with constants as given in Table 1.

In a similar manner, with 12 hours boiling of 40.7 g (0.27 mole) of triethylchlorosilane with 5.57 g (0.09 mole) of H_3BO_3, 8.9 g (24.5%) of tris(triethylsilyl) borate was obtained, of b.p. 178-179° (13 mm).

Reaction of tri-n-butyl borate with triethylsilanol. A mixture of 9.2 g (0.04 mole) of tributyl borate, 16.0 g (0.121 mole) of triethylsilanol, and 0.2 g of sodium was subjected to slow distillation. Below 120°, 6.5 g distilled off. With further fractional distillation 3.8 g was obtained of tris(triethylsilyl) borate. B.p. 142-149° (4 mm), n_D^{20} 1.4342. Yield 23.5%.

Found %: B 2.72, 2.73. $C_{18}H_{45}BO_3Si_3$. Calculated %: B 2.67.

Reaction of tri-n-butyl borate with triethylchlorosilane. A mixture of 30.2 g (0.2 mole) of triethylchlorosilane, 13.8 g (0.06 mole) tributyl borate, and 0.3 g anhydrous $FeCl_3$ was slowly distilled from a fractionation flask. At 76-84° 11.0 g butyl chloride came over. Further fractional distillation in vacuum gave 2.5 g (10%) of tris(triethylsilyl) borate. B.p. 120-130° (1 mm), n_D^{20} 1.4360.

Found %: B 2.64; 2.63. Calculated %: B 2.67.

Reaction of dimethyldiethoxysilane with $B(OH)_3$. By slow distillation of 22.3 g (0.15 mole) of dimethyldiethoxysilane with 3.1 g (0.05 mole) of boric acid, at 78-80°, 12.3 g (0.27 mole) of ethyl alcohol distilled off, and at 116-126°, 4.5 g (0.03 mole) of triethyl borate. The viscous, colorless, tough polymer remaining in the flask was readily soluble in CCl_4, dioxane, and benzene mixed with ether. Ether was distilled off from the pre-filtered ether solution, and the residue freed from volatile products by heating in vacuum.

Found %: B 4.14, 4.32. $[B_2O_3 \cdot 6(CH_3)_2SiO]_n$. Calculated %: B 4.21.

Reaction of methyltriethoxysilane with $B(OH)_3$. 53.5 g (0.3 mole) of methyltriethoxysilane was distilled over 18.6 g (0.3 mole) of boric acid. At 78-79°, 40.0 g of ethyl alcohol distilled off, i.e., 97% of theoretical. In the residue was a solid, nonvolatile and insoluble polymer. It was washed with boiling dioxane and dried in vacuum.

Found %: B 5.40, 5.17. $[B_2O_3 \cdot 4CH_3SiO_{1.5}]_n$. Calculated %: B 5.34.

Reaction of tetraethoxysilane with $B(OH)_3$. By distilling 62.5 g (0.3 mole) of the silico-ethyl ether over 24.7 g (0.4 mole) of boric acid, at 77-79°, 49.1 g of ethyl alcohol came over, i.e., 89% of theoretical. The solid white residue, after extraction with boiling ether and heating in vacuum contained 5.0% B and 28.9% Si.

After further extraction with boiling ethyl alcohol the boron content fell to 0.5%, but the silicon content rose to 36.0%. On calcining, the reaction product, extracted with ether and methanol at 800-900° lost weight by 19.0%, evidently indicating the presence of ethoxy groups.

The reaction of trimethylethoxysilane with $B(OH)_3$. A mixture of 35.5 g (0.3 mole) of trimethylethoxysilane with 6.2 g (0.1 mole) boric acid was heated to boiling point for 6 hrs. After this the b.p. of the reaction mixture rose from 74 to 77°. By fractional distillation 11.4 g was obtained of a mixture of trimethylethoxysilane and ethyl alcohol of b.p. 70-71.5°, n_D^{20} 1.3732; 7.5 g of a mixture of trimethylethoxysilane with hexamethyldisiloxane of b.p. 71.5-100.5°, n_D^{20} 1.3741 and 20 g of crude triethyl borates of b.p. 100-130°, n_D^{20} 1.3792 which, after second distillation had a b.p. of 119.0 (762 mm), n_D^{20} 1.3772.

Found %: B 6.45, 6.47. Calculated %: B 7.41.

The same products, but in other proportions, were obtained by continuing the reaction for 24 hours.

By repeating the experiment under the same conditions for 6 to 48 hours, but in the presence of 0.2 g p-toluenesulfonic acid, besides the above-mentioned reaction products, not more than 1-2 g (3-7%) of tris(trimethylsilyl) borates was also formed.

By prolonged boiling of $(CH_3)_3SiOCH_3$ with boric acid the formation of substances of b.p. above 67° was not observed.

The synthesis of trimethyl borate. 137.0 g (0.9 mole) of tetramethoxysilane was distilled with stirring over 34.8 g (0.5 mole) finely ground boric oxide. At 66-68°, 66.5 g of trimethyl borate distilled over – at 120-121°, 9 g of unreacted $Si(OCH_3)_4$. Yield of $B(OCH_3)_3$ was 62% reckoned on the silico-methyl ether entering into reaction. After a second distillation the trimethyl borate had b.p. of 67.3° (757 mm); n_D^{20} 1.3572 which corresponds very well with literature data.

Found %: B 10.51, 10.14. Calculated %: B 10.41.

Reaction of dimethyldichlorosilane with $B(OH)_3$. 12.4 g (0.2 mole) of boric acid and 38.7 g (0.3 mole) of dimethyldichlorosilane were heated in a reflux condenser until separation of hydrogen chloride ceased. The reaction product, a viscous colorless polymer, was dissolved in ether. After filtration the ether was distilled from the solution, and the residue heated in vacuum.

Found %: B 8.9; Si 26.0. $[B_2O_3 \cdot 3(CH_3)_2SiO]_n$. Calculated %: B 7.41; Si 28.84.

The polymer solidifies in air and becomes coated with a white dense film, with the properties of "bouncing putty" [18].

Cleavage of tris(triethylsilyl) borate with ferric chloride. 5.6 g (0.014 mole) of tris(triethylsilyl) borate was distilled with 0.3 g anhydrous $FeCl_3$. At 220-230°, 3.2 g (62%) hexaethyldisiloxane came over, having n_D^{20} 1.4330.

Found %: Si 22.59, 23.05. $C_{12}H_{30}OSi_2$. Calculated %: Si 22.79.

SUMMARY

Methods have been developed for synthesizing tris(trialkylsilyl) borates and polyboraorganosiloxanes. The four described tris(trialkylsilyl) borates were also synthesized in different ways.

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NEW SYNTHESIS METHODS FOR TRIS(TRIALKYLSILYL) PHOSPHATES

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Researches relating to silicoorganic compounds having phosphorus in their composition are fairly numerous [1-15]. A great part of these researches [1-10] is concerned with compounds including the bond Si–O–P, which, evidently, are also formed as intermediate products under the action of phosphorus halides on hexaalkyldisilozanes [15-17] and alkoxysilanes [10, 18-25]; and also in the production of polyorganosiloxanes by action of phosphoric acid on alkylalkoxysilanes [26].

The only method described in the literature for the synthesis of silicoorganic esters of phosphoric acid – tris(trialkylsilyl) phosphates – is the reaction of hexaalkyldisiloxanes with phosphorus pentoxide [7] according to equation $P_2O_5 + 3R_3SiOSiR_3 \rightarrow 2(R_3SiO)_3PO$.

In the present work new methods are proposed for the synthesis of the above-named esters. We have found that trialkylalkoxysilanes (preferably methoxy derivatives) react smoothly with orthophosphoric acid according to scheme: $3R_3SiOR' + (HO)_3PO \rightarrow 3R'OH + (R_3SiO)_3PO$ forming, (with yields up to 75%) the corresponding tris(trialkylsilyl) phosphates. Reaction is accomplished by simple distillation of the corresponding trialkylalkoxysilane, used in excess, over crystalline orthophosphoric acid. In this way, alcohol is first distilled off, after which the tris(trialkylsilyl) phosphate formed is separated by distillation in vacuum.

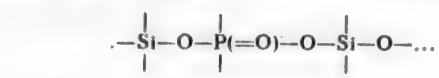
Another simple and convenient method of synthesizing trialkylsilyl esters of orthophosphoric acid is based on heating this acid with trialkylchlorosilane until separation of hydrogen chloride stops. The reaction proceeds as per equation $3R_3SiCl + (HO)_3PO \rightarrow 3HCl + (R_3SiO)_3PO$. The yields of tris(trialkylsilyl) phosphates in this case are lower, and the amount to 35-50%.

In both the above-named methods of synthesizing tris(trialkylsilyl) phosphates the corresponding hexaalkyldisiloxanes are obtained in addition. Their formation, evidently, is facilitated not only by the possible content of water in the initial orthophosphoric acid, but also by the parallel reaction of its dehydration into pyrophosphoric acid.

Finally, we have shown that tris(trialkylsilyl) phosphates may be easily obtained by reacting trialkylhalosilanes with trialkylphosphates, according to equation: $3R_3SiX + (R'O)_3PO \rightarrow 3R'X + (R_3SiO)_3PO$. Trialkylbromosilanes react in the direction indicated in the absence of any catalysts, wherein the yields of tris(trialkylsilyl) phosphates amount to about 65%. Unlike the bromides the trialkylchlorosilanes react with trialkyl phosphates only in the presence of a catalyst, such as anhydrous ferric chloride. Yields of tris(trialkylsilyl) phosphates in this case prove to be lower (40-50%).

The physical constants, analytical data, and yields of the tris(trialkylsilyl) phosphates obtained by us are given in the table. They are colorless viscous liquids, of slight and agreeable odor completely stable at temperatures up to 250-300°. They are hydrolyzed by water, especially with aqueous solutions of strong acids, and accompanied by formation of phosphoric acid that we used for their quantitative analysis. Tris(trialkylsilyl) phosphates are split up by sodium bromide with formation of the corresponding trialkylbromosilanes by hexaalkyldisiloxanes.

The above-indicated methods of synthesizing tris(trialkylsilyl) phosphates may be used also for obtaining various phosphosilicoorganic polymers, with the grouping:



Tris(trialkylsilyl) Phosphates

$(R_3SiO)_3PO$	B.p. (pressure in mm)	d_4^{20}	n_D^{20}	P content (in %)		Si content (in %)		Yield (in %)
				Found	Calc.	Found	Calc.	
$[(CH_3)_3SiO]_3PO$	91—93° (5)	0.9650	1.4082	9.83, 9.82	9.85	26.64, 26.50	26.79	35*
$[CH_3(C_2H_5)_2SiO]_3PO$	145—147 (1)	0.9474	1.4302	7.58, 7.57	7.77	20.9, 20.4	21.13	40**
$[(C_2H_5)_3SiO]_3PO$	183—186 (3)	0.9668	1.4455	7.11, 7.13	7.03	18.7, 18.6	19.12	74**
$[CH_3(n\text{-}C_3H_7)_2SiO]_3PO$	221—224 (10)	0.9326	1.4380	6.45, 6.60	6.41	17.3, 17.1	17.45	50**

In this case, in reacting with orthophosphoric acid (or its esters) the di- or tri-functional derivatives are introduced of the type R_2SiX_2 or $RSiX_3$, where X is a halogen (OCH_3) etc. Thus, for example, in heating orthophosphoric acid with dimethyldichlorosilane, chosen in the molar ratio of 2 : 3, until HCl formation stops, a highly viscous transparent phosphosilicoorganic polymer is formed, soluble in the usual organic solvents, and containing 19% P. The reaction may be generally formulated as follows:

$$3n\,(CH_3)_2SiCl_2 + 2n\,(HO)_3PO \rightarrow 6n\,HCl + \\ + \{\,[(CH_3)_2Si]_3(PO_4)_2\,\}_n$$

The study of the different polymers we have obtained continues.

EXPERIMENTAL

The initial reactions. Trialkylmethoxysilanes are obtained by reacting the corresponding trialkylsilanes with methyl alcohol in the presence of CH_3ONa [27]. Trialkylhalosilanes are prepared by reacting hexaalkyldisiloxanes with the corresponding aluminum halide [28]. Triethyl phosphate is synthesized by reacting $POCl_3$ (obtained with a yield of 81% by hydrolyzing PCl_5) with ethyl alcohol in the presence of pyridine. All the initial reagents were purified by column distillation of 15 theoretical plate efficiency. Crystalline orthophosphoric acid – commercial chemically pure preparation – was held in the desiccator over anhydrous $CaCl_2$.

Analysis: The phosphorus in tris(trialkylsilyl) phosphates was determined as phosphoric acid formed by hydrolysis of these phosphates in an aqueous dioxane medium, which was titrated as a monobasic acid with 0.2 N NaOH, (with bromophenol blue as indicator). Silicon was found as the difference from sum of oxides ($SiO_2 + P_2O_5$), formed by mineralizing with mixed oleum and nitric acid with subsequent heating at 900°, and the P_2O_5 content found alkylimetrically.

Preparation of tris(triethylsilyl) phosphate from $(C_2H_5)_3SiOCH_3$ and H_3PO_4. 58.5 g (0.4 mole) of triethylmethoxysilane was slowly distilled over 9.8 g (0.1 mole) o-phosphoric acid. At 64-66°, 10.8 g methyl alcohol distilled over, i.e., practically theoretical. Further fractional distillation in vacuum gave 32.7 g (74%) of tris-(triethylsilyl) phosphate of b.p. 197-200° (5 mm), n_D^{20} 1.4448 with constants, after second distillation, as given in the table. Besides this, 15.3 g was obtained of hexaethyldisiloxane of b.p. 100-110° (5 mm), n_D^{20} 1.4330.

By a similar method we also prepared $[CH_3(C_2H_5)_2SiO]_3PO$ and $[CH_3(n\text{-}C_3H_7)_2SiO]_3PO$ (Cf. table).

Synthesis of tris(trimethylsilyl) phosphate from $(CH_3)_3SiCl$ and H_3PO_4. 66.3 g (0.61 mole) of trimethylchlorosilane and 19.1 g (0.195 mole) of o-phosphoric acid were boiled in a reflux condenser for 6 hours until HCl separation stopped. B.p. of the reacting mixture then rose to 120°. By fractional distillation 21.5 g (35%) of crude tris(trimethylsilyl) phosphate was obtained of b.p. 190-235°, n_D^{20} 1.4080, which, after a second distillation, had constants as given in the table. Moreover, we also obtained 35 g of hexamethyldisiloxane of b.p. 96-101°.

Synthesis of tris(triethylsilyl) phosphate from $(C_2H_5)_3SiBr$ and $(C_2H_5O)_3PO$. In distilling a mixture of 17.3 g (0.095 mole) of triethyl phosphate and 60.5 g (0.31 mole) triethylbromosilane, 21.5 g (70%) of ethyl bromide came over at 38-40°. By fractional distillation of the residue in vacuum we obtained 26.7 g (64%) of tris(triethylsilyl) phosphate of b.p. 240-243° (20 mm), n_D^{20} 1.4461, d_4^{20} 0.9669.

Found %: P 7.26, 7.27. Calculated %: P 7.03.

Synthesis of tris(triethylsilyl) phosphate from $(C_2H_5)_3SiCl$ and $(C_2H_5O)_3PO$. 22.6 g (0.15 mole) triethylchlorosilane, 9.1 g (0.05 mole) of triethyl phosphate, and 0.2 g anhydrous $FeCl_3$ were heated in a reflux condenser for 9 hours until hydrogen chloride ceased forming. With fractional vacuum distillation of the reaction mixture 9.0 g (41%) was obtained of tris(triethylsilyl) phosphate, with b.p. 210-225° (13 mm), n_D^{20} 1.4458, which after redistillation had b.p. 220-225° (13 mm), n_D^{20} 1.4458.

Found %: P 6.78, 6.80. $C_{18}H_{45}O_4PSi_3$. Calculated %: P 7.03.

Reaction of dimethyldichlorsilane with o-phosphoric acid. 38.7 g (0.3 mole) of dimethyldichlorsilane and 19.6 g (0.2 mole) of o-phosphoric acid were heated for 6 hours under the usual pressure and 4 hours in vacuum until hydrogen chloride separation stopped. The reaction product was a highly viscous polymer, soluble in organic solvents, and hydrolyzed with water.

Found %: P 18.8, 18.9, approximating to composition $[(CH_3)_2Si]_3(PO_4)_2$. Calculated %: P 17.00).

SUMMARY

It has been shown that tris(trialkylsilyl) phosphates may be synthesized by the following methods: 1) Reaction of orthophosphoric acid with trialkylalkoxysilanes; 2) reaction of trialkylchlorosilanes with orthophosphoric acid; 3) reaction of trialkyl phosphates with trialkylhalogensilanes. By similar means there may also be obtained various phosphosilicoorganic polymers containing alternating atoms of silicon, oxygen, and phosphorus. Four tris(trialkylsilyl) phosphates have been synthesized and described, two of which were not previously known.

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THE OZONIZATION OF UNSATURATED COMPOUNDS

III. THE ADDITION OF OZONE TO INTERNAL AND EXTERNAL DOUBLE BONDS IN DIVINYL RUBBER

A. I. Yakubchik, N. G. Kasatkina and T. E. Pavlovskaya

We have previously shown [1] that the components of a mixture of ethylene compounds with different degrees of substitution are ozonized simultaneously and the curves of the absorption of ozone by mixtures of this type do not show breaks. The curves of ozone absorption by divinyl rubbers in whose molecule the internal double bond* corresponds to the doubly-substituted ethylene bond type and the external double bond to the monosubstituted ethylene bond type, also do not show breaks (Fig. 1, Curves 1-4).

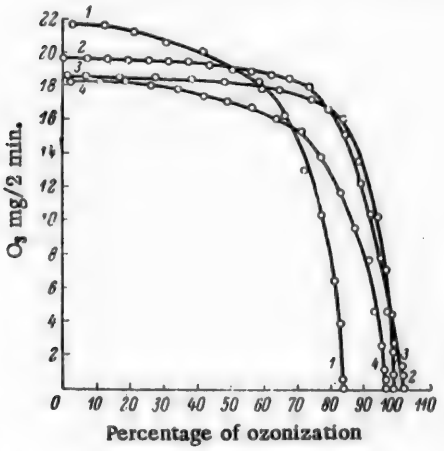


Fig. 1. Curves of ozone absorption by divinyl rubbers.
I) The rubber contains links with external double bonds: 1) 36%, 2) 52%, 3) 45%, 4) 50%.

TABLE 1

Sector	Percentage of double bonds which added ozone	
	external bonds	internal bonds
I	12	13
II	17	9
III	17	7
IV	0	25

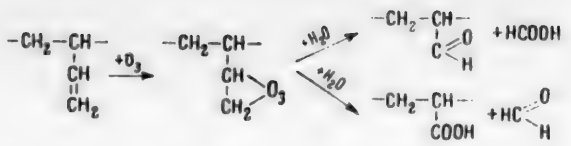
To ascertain whether the internal and external double bonds ozonize successively or simultaneously and, in the latter event, in what amounts and ratios they participate in ozonization, experiments were carried out on the complete and partial ozonization of sodium-divinyl rubber with subsequent determination of the external double bonds which had added ozone.

Sodium-divinyl rubber was ozonized 25, 50, 75 and 100% (Fig. 1, Curve 3). The ozonides were decomposed and the amount of formic acid and formaldehyde in the decomposition products was determined. The equivalent amount of ozone added to the external double bond was calculated from the amount of formic acid and formaldehyde found.

* The link of divinyl rubber with an internal double bond is

$$-CH_2-CH=CH-CH_2-;$$

the link of divinyl rubber with an external double bond is $-CH_2-CH-$
$\quad\quad\quad



The amount of ozone added to the internal double bonds was calculated from the difference between the total amount of ozone added and that which was added to the external double bonds.

If the curve of the absorption of ozone by sodium-divinyl rubber is divided into four sectors according to the amount of ozone added i.e., I – 25% ozonization, II – 25 to 50%, III – 50 to 75%, IV – 75 to 100%, the analytical results may be given in the form of Table 1.

The addition of ozone to the external double bonds takes place in Sectors I, II and III. Ozone is added simultaneously to the internal double bonds. In sector IV the addition capacity of the external double bonds is exhausted. Although the investigated rubber contains rather more internal double bonds than external, the ozonization of the latter is completed first; external bonds are evidently ozonized in preference to the internal bonds.

EXPERIMENTAL

The investigated rubber was obtained by polymerization of divinyl at room temperature in the presence of 0.5% sodium metal. The divinyl was obtained from its tetrabromide by the action of zinc in aqueous alcohol. The sodium-divinyl rubber was purified by dissolving twice in benzene and precipitating twice with ethyl alcohol. Four ozonization tests were carried out using rubber purified and dried to constant weight with subsequent calculation of the formic acid and formaldehyde in the ozonization products.

The method for the ozonization of unsaturated compounds has been previously described [2]. Ozonization was carried out in chloroform at 0°. The ozone was passed through a rubber solution at a constant rate of 7 liters per hour. The amount of ozone added was calculated from the absorption curves, the latter being drawn simultaneously with the ozonization process. The rubber was first ozonized to completion, i.e., until the results of the titration of the initial and final samples of iodine precipitated by the ozone from a solution of potassium iodide coincided [2]. This amount of ozone absorbed by the rubber was taken as 100%. Twenty-five, 50 and 75% of this amount of ozone was calculated and added to various weight samples of rubber in the other experiments. The chloroform was distilled off from the ozonide under reduced pressure to constant weight. The ozonides were decomposed by a 10-fold amount of water with heating to 100° in a water bath. The electrical conductivity of the solution of the decomposition products was determined during the process of decomposition of the rubber ozonides. With increasing decomposition of the ozonide the electrical conductivity of the solution of the decomposition products increased as a result of the formation of acids. When the ozonide had been completely decomposed the electrical conductivity became constant. The samples used for the determination of electrical conductivity were taken by means of a siphon connecting the decomposition flask to a buret in which an identical volume of solution was sampled in each instance. The determination was carried out at 18° in a vessel with platinum electrodes placed in an ultrathermostat. The vessel was connected up to the usual circuit for determining electrical conductivity. The formaldehyde in the products of the ozonolysis of rubber, ozonized 25, 50, 75 and 100%, was quantitatively determined from its condensation product with β-naphthol [3] and the formic acid was determined by the calomel method [4]. The results are given in Table 2.

TABLE 2

Percentage of ozonization	Weight (in g)				Ozone added to double bonds		Percentage of ozone in the double bonds	
	Rubber	Added ozone	formaldehyde	formic acid	external	internal	external	internal
25.2	4.20	0.94	0.0288, 0.0290	0.3679, 0.3687	0.44	0.50	11.8	13.4
51.2	4.27	1.94	0.0847, 0.0861	0.8944, 0.8931	1.08	0.86	28.5	22.7
74.9	3.19	2.12	0.1472, 0.1547	1.0763, 0.9982	1.28	0.84	45.2	29.7
100.0	3.21	2.85	0.1027, 0.1032	1.0663, 1.0560	1.28	1.57	44.9	55.1

The ozonization of the external double bonds in the sodium-divinyl rubber is completed when about 75% of the rubber has been ozonized.

SUMMARY

1. It was established that the curves of ozone absorption by divinyl rubbers do not show breaks.

2. Sodium-divinyl rubber was ozonized 25,50, 75 and 100%. From the quantitative determination of the external double bonds which add ozone it was established that there is no strict selectivity in the ozonization of the double bonds of rubber: the external double bonds are ozonized more rapidly than the internal and their ozonization is completed earlier than the ozonization of the internal double bonds.

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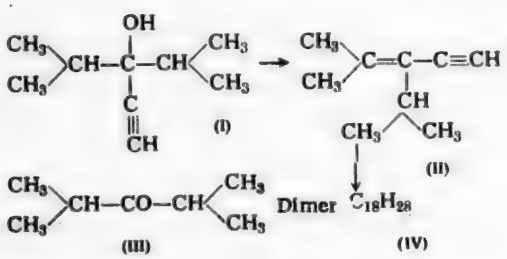
HOMOLOGS OF MONOVINYLACETYLENE

V. DIMERIZATION OF VINYLACETYLENE HYDROCARBONS UNDER CONDITIONS OF THE DEHYDRATION OF ACETYLENE ALCOHOLS

I. A. Favorskaya, Yu. P. Artsybasheva and L. V. Fedorova

Developing the initial experiments made by the student A. Zderko we established in the present work, together with Yu. P. Artsybasheva, that as a result of the dehydration of diisopropylacetylenylcarbinol (I) over unbaked porcelain at 300° in a current of CO_2, monomeric hydrocarbons (II) are obtained in low yield (3-5%) and the principal reaction product with a yield of about 60% is a dimer of the hydrocarbon (IV).

The initial carbinol and insignificant amounts (3-5%) of diisopropylketone (III) were also found in the dehydration products.



In this investigation L. F. Fedorova also isolated a dimeric hydrocarbon with a yield of about 10% in the dehydration of methyl-n-butylacetylenylcarbinol over unbaked porcelain.

By oxidation with permanganate in an alkali medium, a mixture of aromatic acids which were identified by means of their silver salts was obtained. The structure of a substituted styrene was attributed to the dimer on the basis of these results.

Table 1 gives the experimental data on the dehydration of some acetylene alcohols.

The experimental data and those available from literature were very limited; it is evident from Table 1, however, that for enoid hydrocarbons the tendency to form dimers increases with substitution at the terminal hydrocarbon atoms of the double bond.

In literature, styrene dimerization of vinylacetylene hydrocarbons is regarded as a similar reaction to a Diels-Alder condensation. Dykstra [4] suggested a system for the styrene dimerization of vinylacetylene based on addition at the 1,2 and 1,4 positions with the intermediate formation of cyclohexatriene with an allene structure; A. E. Favorsky [5] suggested that dimerization precedes the isomerization of the vinylacetylene under the influence of high temperature in a "molecule with unsaturated carbon atoms at the terminal positions" (biradical).

It is known with regard to the diene synthesis reaction that substitution in the 1,4 position of the diene system impedes the reaction; in addition, the spatial configuration of the substitutes has an influence as was

Dimerization of Enoid Hydrocarbons Under Dehydration Conditions

Carbinol	Catalyst	Temperature	Hydrocarbon	Yield of hydrocarbon (as %)	Yield of dimer (as %)
Diisopropylacetylenylcarbinol	Unbaked porcelain	300°	4-Methyl-3'-metho-3-3-ethylpenten-1-yne	3-5	60
Methyl-n-propylacetylenylcarbinol [1, 2]	$MgSO_4$	230	Mixture of 3-3-methylhexen-1-yne and 3-methen-3-hexen-1-yne in the ratio of 1 : 2	67	Negligible amount of dimer
Methylbutylacetylenylcarbinol	Unbaked porcelain	240	Mixture of 3-methen-1-heptin and 3-methyl-3-hepten-1-yne	50	10
Dimethylacetylenylcarbinol	$MgSO_4$	245	2-Methyl-3-buten-1-yne	65	Formation of dimer not noted
Methyl-tertiaryacetylenylcarbinol [3].	$MgSO_4$	300	α-Tertiarybutylvinylacetylene	70	Formation of dimer not noted

shown in the example of piperylene, only the trans- form takes part in the reaction [6, 7]; α,α-substituted dienes cannot add dienophyllic compounds.

All attempts to introduce 4-methyl-1,3-pentadiene in diene condensation were unsuccessful [8].

The structural factors which favor the styrene dimerization of enoid hydrocarbons evidently have the reverse influence on the capacity of diene hydrocarbons to take part in the Diels-Alder reaction.

In the present instance, during the study of the dehydration products of diisopropylacetylenylcarbinol principal attention was paid to the characteristics and structural proof of the dimer of the hydrocarbon.

Proceeding from A. E. Favorsky's system of the dimer, the structure of a substituted styrene or a substituted cyclooctatetraene may be assumed; two isomers, depending on the orientation of the hydrocarbon molecules, are possible in each instance.

Two fractions, in the ratio of 1 : 5, were separated by distilling the dimer in a fractionating column under high vacuum; by their elementary composition and molecular weight these fractions corresponded to the formula $C_{16}H_{28}$ for the dimer of an enoid hydrocarbon.

As a result of the spectroscopic investigation of both fractions of the dimer (IV) in the ultraviolet and infrared regions of the spectrum it was found that their absorption curves are of different character. For the main fraction of the dimer with n_D^{20} 1.5178 the position of maximum absorption and the extinction coefficient in the ultraviolet coincide with the corresponding values for substituted styrenes [9] (curve 1, Fig. 1).

In the case of the first fraction of the dimer with a refractive index of 1.5080 the smoothness of the absorption curve [2] in the 240-270 mμ region indicates the absence of aromatic compounds and open-chain polyenes [10] (curve 2, Fig. 1).

The absorption curves for cyclooctatriene in the ultraviolet, found by Reppe [11] and Cope [12], have a similar character.

The absorption curves in the 5-6 μ region were determined for both fractions on an IKS-11* spectrometer (Fig. 2).

The presence of a maximum of 6.25 μ (1600 cm^{-1}) (curve 1, Fig. 2) again confirms the aromatic character of the hydrocarbon [13]. The investigation of the infrared absorption spectra in the 2000-1650 cm^{-1} region is one of the most effective methods of determining the nature of the substitution in the benzene ring [13].

According to Joung's data [14] it may be assumed that the main fraction of the dimer (n_D^{20} 1.5178) (curve 1, Fig. 2) contains a hydrocarbon which is a 1, 2, 3, 5, substituted benzene (5.88 μ, 1705 cm^{-1}). The reservation must, however, be made that Joung's data refer to substitutes of a simpler character.

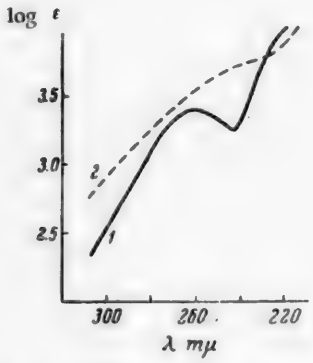


Fig. 1. Absorption curves in the ultraviolet of the dimers 4-methyl-3'-metho-3-3-ethylpenten-1-yne.
1) Dimer with n_D^{20} 1.5178 with 0.002161-0.0001798 m, λ_{max} 266 mμ, log ϵ 3.37; 2) dimer with n_D^{20} 1.5080 with 0.00274-0.0006 m.

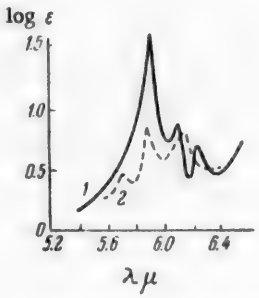
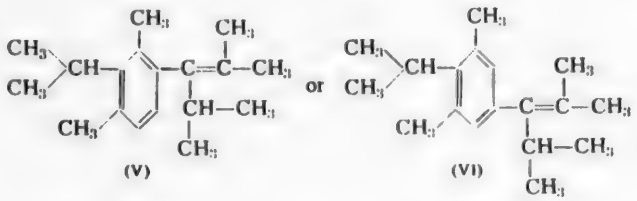


Fig. 2. Absorption curves in the infrared region of the spectrum of the dimers 4-methyl-3'-metho -3-3 ethylpenten-1-yne. 1) Dimer with n_D^{20} 1.5178: λ_{max} 5.88 μ (1705 cm^{-1}), 6.09 μ (1641 cm^{-1}, 6.25 μ (1600 cm^{-1}); 2) dimer with n_D^{20} 1.5080: λ_{max} 5.70 μ (1755 cm^{-1}), 5.88 μ (1705 cm^{-1}), 6.13 μ (1632 cm^{-1}).

Like the absorption curve in the ultraviolet, curve 2 (Fig. 2) for the dimer fraction (n_D^{20} 1.5080) confirms the nonaromatic character of the hydrocarbon. The spectrum in the 3-5 μ region was determined for both fractions in order to establish that the dimer could not possibly have a structure with a cyclobutane ring and a triple bond [4] owing to addition at the double bond. The absence of a maximum in the 4-5 μ region, which is a characteristic of a triple bond, excludes the possibility of this structure.

On the basis of the data of spectroscopic investigations and the relative dispersion [15] (see EXPERIMENTAL) it may be safely assumed that the fraction with n_D^{20} 1.5178 contains the dimer of an enoid hydrocarbon 4-methyl-3-metho-3-3-ethylpenten-1-yne of the styrene type (V or VI).



As regards the dimer fraction with n_D^{20} 1.5080 it might appear from the above-mentioned data that the conclusion could be drawn that the fraction contains a hydrocarbon corresponding in structure to cyclopolyolefine,

* The prism was of rock salt with a maximum slot and a layer of 0.1 mm.

a derivative of cyclooctatetraene. Side by side with data confirming this assumption there were a number of factors, however, which, although they did not disprove the main conclusion, made the purity of the hydrocarbon obtained questionable.

The dimer obtained directly in the dehydration process may contain the condensation products of a ketone which is formed by the partial decomposition of acetylene alcohols over Al_2O_3. In oder to establish the absence of condensation products of diisopropylketone we showed by means of a special experiment that under dehydration conditions diisopropylketone which is not condensed is mainly recovered.

In addition to the main ketone fraction recovered, a slight amount (0.5 g) of a substance with n_D^{20} 1.4141 with a b.p. considerably below that of the dimer was obtained. This fraction gave a precipitate with 2,4-dinitrophenylhydrazine and had a maximum at 280 mμ [16], characteristic of a carbonyl. A slight admixture of the condensation products of the ketone could, however, have been contained in the first fraction of the dimer. This supposition is confirmed by the following facts: in the infrared region of the spectrum there is a maximum at λ 2.85 μ, characteristic of a hydroxyl group; the determination of the active hydrogen by Terentyev's method showed 0.5% hydroxyl group. Spectroscopic determination of traces of the carbonyl group [17] indicates that this fraction contains 0.4% of a carbonyl-containing substance.

On the basis of these data it may be assumed that the fraction with n_D^{20} 1.5080 contains an admixture of several percent of the condensation products of a ketone. Evidently, as a result of the presence of this admixture which forms an azeotropic mixture, we were able to isolate a hydrocarbon fraction with n_D^{20} 1.5080 which did not contain a dimer of the styrene type.

EXPERIMENTAL

I. Dehydration of methyl-n-butylacetylenylcarbinol.

Methyl-n-butylacetylenylcarbinol was determined by A. E. Favorsky's method. The yield was 60%. The b.p. was 62-63° (15 mm), n_D^{20} 1.4360.

Dehydration was carried out by passing the carbonyl vapor in an atmosphere of CO_2 through a tube filled with unbaked porcelain. The dehydration temperature was 220-240°. The hydrocarbon yield was 50%. The yield of the dimer was 10%. The hydrocarbon was a colorless mobile liquid.

B.p. 44-45° (50 mm), n_D^{20} 1.4395, d_4^{20} 0.776, MR_D^{20} 36.90; calc. 36.67.
Found %: C 88.52, 88.78; H 11.12, 10.98. M 108.4. C_8H_{12}. Calculated %: C 88.83; H 11.18. M 108.

The dimer was a viscous yellowish liquid. The reaction for free acetylene hydrogen was negative. The following fractions were obtained by distillation of the isomer:

1st 106-112° (2 mm), n_D^{20} 1.5032; 2nd 113-115° (2 mm), n_D^{20} 1.5100; 3rd 114-115° (1.5 mm), n_D^{20} 1.5178, d_4^{20} 0.9125, MR_D 71.88; calc. 72.02.
Found (3rd fraction) %: C 89.18; H 10.72. M 215. $C_{16}H_{24}$. Calculated %: C 88.83 ; H 11.18. M 216.

2 g of the dimer with a b.p. of 113-115° (2.0 mm) was oxidized. 0.7 g of nonvolatile acids was obtained as a result of oxidation; after standing in a vacuum desiccator for three days these acids were completely uncrystallized. The silver salts were obtained from 0.7 g of the acids.

Found %: Ag 55.70 (I precipitation); 56.59 (II precipitation). $C_6H_3(COOAg)_3$. Calculated %: Ag 61.01. $CH_3C_6H_4(COOAg)_2$. Calculated %: Ag 54.80.

II. Dehydration of diisopropylacetylenylcarbinol.

The diisopropylacetylenylcarbinol was synthesized by A. E. Favorsky's method.

B.p. 80° (45 mm), n_D^{20} 1.4452, d_4^{20} 0.8718, MR_D 42.76; calc. 43.09.

60 g of diisopropylacetylenylcarbinol was passed for 24 hours in an atmosphere of CO_2 through a tube filled with unbaked porcelain at 300-320°. The dehydration products were collected in a receiver cooled with

ice. The aqueous layer was separated and the products were dried with potash and distilled under vacuum. The following fractions were obtained by distillation with a fractionating column:

1st 41° (30 mm), 1.30 g (hydrocarbon); 2nd 32-35° (25 mm), n_D^{20} 1.4193, 2.57 g (ketone); 3rd 68-71° (25 mm), n_D^{20} 1.4451, 31.7 g (carbinol); residue 17 g (dimer (60%).

The 1st fraction gives a deposit with an ammoniacal solution of silver oxide.

n_D^{20} 1.4532, d_4^{20} 0.7916, MR_D 41.59. $C_9H_{14}F_4$. Calculated 41.29.
Found %: C 88.10; H 10.83. C_9H_{14}. Calculated %: C 88.45; H 11.54.

The 2nd fraction – diisopropylketone gave a 2,4-dinitrophenylhydrazone with a m.p. of 93°. A mixed melt of a sample of this compound with the 2,4-dinitrophenylhydrazone of diisopropylketone showed no depression of the m.p.

Examination of the dimer (IV). The following three fractions of the dimer were obtained by fractional distillation under high vacuum. The absorption curves for the 1st and 3rd fractions were taken on an SF-4 spectrophotometer and an IKS-11 spectrometer. The curves are given in the general section.

The dimer was a viscous liquid with a golden yellow color. The carbonyl group content of the 1st fraction was determined. The precipitate of the 2,4-dinitrophenylhydrazone does not separate out on long standing.

1st fraction: b.p. 116-119° (3 mm), n_D^{20} 1.5080, d_4^{20} 0.8990, MR_D 81.02. $C_{18}H_{28}F_4$. Calculated 81.25. Relative dispersion 27.4 [15].
Found %: C 88.17, 88.48; H 11.39, 11.71. M 224. $C_{18}H_{28}$. Calculated %: C 88.45; H 11.54. M 244.4.

2nd fraction: b.p. 85° (0.05 mm), n_D^{20} 1.5155.
Found %: C 88.46, 88.26; H 11.61, 11.51. $C_{18}H_{28}$. Calculated %: C 88.45; H 11.54.

3rd fraction: b.p. 86° (0.05 mm), n_D^{20} 1.5178, d_4^{20} 0.9160, MR_D 80.82. $C_{18}H_{28}F_4$. Calculated:81.25. Relative dispersion 28.4.
Found %: C 88.09, 88.01; H 11.26, 11.54. M 225. $C_{18}H_{28}$. Calculated %: C 88.45; H 11.54.

The absorption curves for this fraction were taken on an SF-4 spectrophotometer and an IKS-11 spectrometer.

Study of the conversions of diisopropylketone under dehydration conditions. 42 g of diisopropylketone (n_D^{20} 1.3994) was passed in a current of CO_2 through a pipe filled with unbaked porcelain at a temperature of 330°. The products were collected in a receiver cooled with ice. Separation of water was not noted. Two fractions were obtained by distillation with a fractionating column:

1st fraction b.p. 46-50° (40 mm), n_D^{20} 1.4017, 36 g (diisopropylketone): 2nd fraction b.p. 66-70° (40 mm), n_D^{20} 1.4141, 0.5 g.

The 2,4-dinitrophenylhydrazone of the latter fraction was obtained with a b.p. of 91°; a mixed melt with the 2,4-dinitrophenylhydrazone of diisopropylketone did not show any depression of the melting point. The absorption curve for this fraction was taken on an SF-4 spectrophotometer. The curve has a maximum at λ 280 mμ, for the diisopropylketone λ 285 mμ.

SUMMARY

1. In the dehydration of diisopropylacetylenylcarbinol over unbaked porcelain in a current of CO_2 at 300° it was established that the main reaction product obtained is a dimer of the enoid hydrocarbon 4-methyl-3'-metho-3-ethylpenten-1-yne.

2. By the spectroscopic investigation of the fraction of the dimer in the ultraviolet and infrared regions of the spectrum it was found that the dimer is a mixture of two hydrocarbons: a substituted styrene and a non-aromatic type of hydrocarbon, possibly cyclopolyolefine (in a ratio of 5 : 1).

3. As a result of the dehydration of methyl-n-butylacetylenylcarbinol over unbaked porcelain in a current of CO_2 at 240° it was found that 10% of the dimer of an enoid hydrocarbon of the styrene type is formed.

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INVESTIGATIONS IN THE FIELD OF OXIDE ADDITIONS

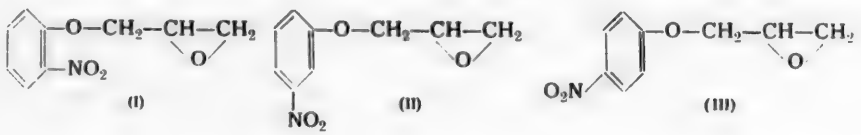
IX. THE INTERACTION OF α-OXIDES OF ALLYL ESTERS OF NITROPHENOLS WITH BENZIMIDAZOLE

I. I. Chizhevskaya and V. I. Pansevich-Kolyada

It was established by investigations on the reaction between ethylene oxide and various amines that, depending on the degree of substitution of the amine group, one, two or three molecules of ethylene oxide can react with one molecule of amine with the formation of primary, secondary and tertiary amine derivatives respectively [1-5]. The reaction takes a similar course in the case of more complex organic α-oxides and also alkyl and aryl esters of glycide with amines [6, 7].

We tried to react benzimidazole with glycidic esters of nitrophenols in order to obtain 1-o-(m-, p-) nitrophenoxy-3-N-benzimidazolido-2-propanols (V-VII) which could be of interest as new physiologically active compounds.

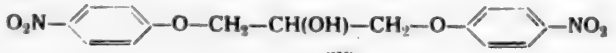
α-Oxides of allyl esters of o-, m- and p-nitrophenols (I-III) were obtained by the interaction of nitrophenols with epichlorhydrin in the presence of an aqueous solution of caustic soda (4.8%) with a yield of 70-80% [8, 9].



(I) (II) (III)

The α-oxides obtained were identical with the previously-described products of the oxidation of allyl esters of nitrophenols by acetylene hydrogen peroxide [10].

In the reaction of epichlorhydrin with p-nitrophenol we obtained two colorless crystalline substances. The first of these (yield 10-15%) had a b.p. of 67° and was the expected α-oxide of the allyl ester of p-nitrophenol (III). The second substance (yield 40-50%) with a b.p. of 145° was found to be 1,3-di-p-nitrophenoxy-2-propanol (IV), described in literature [8-11].



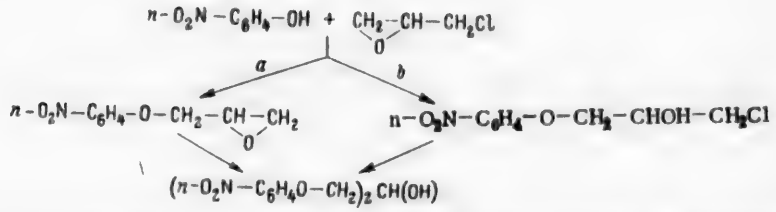
(IV)

Our attempts to increase the yield of the α-oxide of the allyl ester of p-nitrophenol by interacting p-nitrophenol with epichlorhydrin using an increased concentration of alkali (up to 10%), and also by carrying out the reaction with an aqueous solution of the sodium salt of p-nitrophenol, were not successful. The use of caustic potash instead of soda and a higher temperature (60-70°) resulted in an increase in the yield of 1,3-di-p-nitrophenoxy-2-propanol to 60-65% and a reduction in the yield of the α-oxide to 5-7%.

The formation of the product (IV) in the reaction in question may evidently be explained by the higher reactivity of the α-oxide ring of the allyl ester of p-nitrophenol compared with the α-oxides of o- and m-

nitrophenols which did not show similar products when made under analogous conditions.

The formation of the product (IV) can evidently be represented in the following manner

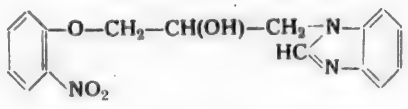


The formation of 1-p-nitrophenoxy-3-chlor-2-propanol was not noted in the case of the interaction of p-nitrophenol with epichlorhydrin in the presence of an aqueous solution of alkali. In consequence, the most probable of the two directions (a and b) is (a).

The interaction of α-oxides of allyl esters of nitrophenols with benzimidazole was carried out by heating these substances in alcohol with the addition of a few drops of pyridine. When the substances were heated without the addition of pyridine the reaction did not take place and when they were heated in a sealed glass tube at 100 and 150° tarring occurred.

The products of the interaction of α-oxides of allyl esters of nitrophenols (I-III) with benzimidazole are crystalline substances soluble in aqueous alkalis and acids.

In accordance with data available in literature [7, 9, 11], the substances we obtained are the nitroderivatives (o-, m-, p-) of 1-phenoxy-3-N-benzimidazolido-2-propanol (V-VII).



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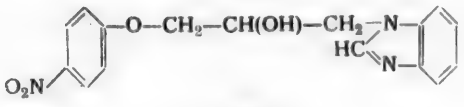
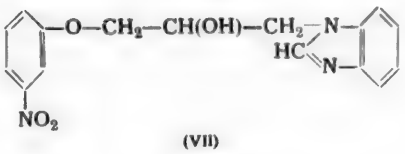


(VI)



(VII)

EXPERIMENTAL

The epichlorhydrin was obtained from the 1,3-dichlorhydrin of glycerin [12].

B.p. 118-119°, n_D^{20} 1.4356, d_4^{25} 1.1730.

The α-oxides of allyl esters of nitrophenols (I, II, III) and 1,3-di-p-nitrophenoxy-2-propanol (IV) were obtained by the method described in literature [7].

(I) M.p. 50-51° (from petroleum ether); (II) m.p. 62-63° (from ether);(III) m.p. 67-68° (from a mixture of methyl and ethyl alcohols); (IV) m.p. 145° (from acetone).

1-o-Nitrophenoxy-3-N-benzimidazolido-2-propanol (V). 4 g of the α-oxide of the allyl ester of o-nitrophenol and 4 g of benzimidazole were heated together with several drops of pyridine for 3-4 hours. After partial distillation of the alcohol a fine crystalline precipitate settled out; this was recrystallized from aqueous methyl alcohol. A finely-crystalline precipitate of a light-yellow color, soluble in acids, was obtained. The m.p. was 174°.

Found %: C 61.47, 61.76; H 4.41, 4.29; N 13.10. $C_{16}H_{15}O_4N_3$. Calculated %: C 61.28; H 4.22; N 13.46.

When gaseous hydrogen chloride was passed into an alcoholic solution of the substance (V) a chlorhydrate was obtained which after recrystallization from a mixture of alcohol and ether melted at 238-239°.

Found %: Cl 10.41, 10.17. $C_{16}H_{16}O_4N_3Cl$. Calculated %: Cl 10.14.

1-m-Nitrophenoxy-3-N-benzimidazolido-2-propanol- (VI). This was obtained in a similar manner to substance (V). The duration of the period of heating was 1.5 hours. The color of the fine crystals was white, almost yellowish. The m.p. was 207° (from alcohol).

Found %: C 61.01, 61.62; H 3.99, 4.39; N 13.60. $C_{16}H_{15}O_4N_3$. Calculated %: C 61.28; H 4.22; N 13.46.

The chlorhydrate was a white crystalline powder with a m.p. of 224-226° (from alcohol).

Found %: Cl 10.22, 10.20. $C_{16}H_{16}O_4N_3Cl$. Calculated %: Cl 10.14.

1-p-Nitrophenoxy-3-N-benzimidazolido-2-propanol (VII). This was obtained in a similar manner to substance (VI). It was a white crystalline powder with a m.p. of 135-136.5°.

Found %: C 61.14, 61.42; H 4.37, 4.27; N 13.11, 13.27. $C_{16}H_{15}O_4N_3$. Calculated %: C 61.28; H 4.22; N 13.46.

The chlorhydrate was a white crystalline powder with a m.p. of 217-219° (decomp).

Found %: Cl 10.05, 9.87. $C_{16}H_{16}O_4N_3Cl$. Calculated %: Cl 10.14.

SUMMARY

1. The interaction of the α-oxides of allyl esters of o-, m- and p-nitrophenols with benzimidazole was studied.

2. Three products of this reaction, not described in literature, were obtained and their characteristics determined: 1-o-nitrophenoxy-3-N-benzimidazolido-2-propanol, 1-m-nitrophenoxy-3-N-benzimidazolido-2-propanol and 1-p-nitrophenoxy-3-N-benzimidazolido-2-propanol.

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INVESTIGATION IN THE FIELD OF GLYCOL ETHERS

XXXI. SYNTHESIS OF γ-HALO ETHERS OF THE ALIPHATIC SERIES

Shamkhal Mamedov

γ-Halo ethers are prepared by various methods [1-5]. A practical method of synthesizing γ-halo ethers is by alkylation of α-halo ethers with ethylenic hydrocarbons in the presence of catalysts.

$$R-CH=CH_2 + \underset{\underset{X}{|}}{CH_2}-O-R' \xrightarrow{ZnCl_2} R-\underset{\underset{X}{|}}{CH}-CH_2-CH_2-O-R'$$

However, the work which has been carried out in this field is still insufficient [6-9]. We set for ourselves the problem of carrying out a systematic investigation of the alkylation of α-halo ethers with ethylenic hydrocarbons, both individual olefins obtained by the dehydration of the corresponding alcohols and fractions of ethylenic hydrocarbons-products of the pyrolysis and cracking of petroleum raw materials.

Simultaneously, we pursued another object, that of studying the alkylation products, i. e., the study of the γ-halo ethers as source materials for new organic syntheses. We paid particular attention to the study of the properties of those γ-halo ethers which can by synthesized from the products of petroleum processing. γ-Chloro ethers and γ-bromo ethers were predominantly studied.

We defined precisely and changed significantly the synthesis conditions, which permitted us to carry out the condensation of α-halo ethers with gaseous ethylenic hydrocarbons without the use of pressure.

Our experiments showed that the activity of the α-halo ethers referred to the same ethylenic hydrocarbon gradually decreased with an increase in the molecular weight of the α-halo ether; i. e., the activity decreased in the order:

$$CH_3-O-CH_2X > C_2H_5-O-CH_2X > C_4H_9-O-CH_2X > C_5H_{11}-O-CH_2X.$$

As regards the activity of the ethylenic hydrocarbons referred to the same halo ether, the reverse was the case-the activity of α-ethylenic hydrocarbons significantly increased with an increase in their molecular weights.

The reaction of α-chlorides on ethylenic hydrocarbons has previously been described as endothermic, requiring heating of the mixture in the neighborhood of 80° [6,7]. However, our experiments showed just the opposite-the reaction of α-halo ethers with ethylenic hydrocarbons in the presence of zinc chloride catalyst is exothermic. The liberation of heat is precisely one reason for the formation of a number of by-products and, to a considerable extent, for the tarring which occurs. Hence, it follows that the reaction must be carried out without heating, at room temperature, and even with cooling of the reaction mixture to 0° in the case of liquid hydrocarbons.

It should be mentioned that the amount of catalyst relative to the amount of α-chloro ether used also has a considerable effect on the formation of by-products. The amount of catalyst required for the ethylenic hydrocarbons studied by us did not exceed 5%. The nature of the α-halo ether also had a substantial effect on the yield of γ-halo ether. As was stated above, an α-chloromethyl ether acts on ethylenic hydrocarbons more vigorously than does an α-chlorobutyl ether.

It would seem, then, that the yield of γ-chloro ether should be greater when an α-chloromethyl ether is used. However, the reverse was observed, which is explained by the fact that the first members of the α-halo ethers (α-halomethyl and α-haloethyl ethers) under the influence of the catalyst ($ZnCl_2$) undergo a deeper change than do the higher members of the α-halo ethers. This change proceeds parallel to the basic course of the reaction and with a higher rate than when higher α-halo ethers are used.

Besides the indicated tarry products, another by-product, which proved to have a higher molecular weight than the basic reaction product – the γ-chloro ether – was isolated from the reaction mixture. The formation of this product is explained by the interaction of the γ-halo ether formed with ethylenic hydrocarbons [8].

$$R{-}CH{=}CH_2 + ClCH(R){-}CH_2{-}CH_2{-}O{-}R' \xrightarrow{ZnCl_2} R{-}CH(Cl){-}CH_2{-}CH(R){-}CH_2{-}CH_2{-}O{-}R$$

Moreover, among the by-products of the synthesis of γ-chloro ethers, there were always observed chlorine derivatives corresponding to the hydrocarbon used in the reaction. The formation of these halogenated hydrocarbons has been explained [8] by the addition of hydrogen halide liberated from the γ-halo ethers under the influence of the catalyst. However, in our opinion, the halogenated hydrocarbons could be formed without decomposition of the γ-halo ethers, since the α-halo ether itself always contains free hydrogen halide, the action of which on the product of the reaction of the catalysts with the ethylenic hydrocarbons [10] could form the halogen derivatives along with the formation of the γ-halo ethers.

$$CH_3{-}CH(Cl){-}CH_2ZnCl \xrightarrow{R{-}O{-}CH_2{-}Cl} CH_3{-}CH(Cl){-}CH_2{-}CH_2{-}O{-}R + ZnCl_2$$

$$CH_3{-}CH(Cl){-}CH_2ZnCl \xrightarrow{HCl} CH_3{-}CH(Cl){-}CH_3 + ZnCl_2$$

We paid particular attention to the course of the addition of α-halo ethers to ethylenic hydrocarbons, because this has a decisive import in establishing the structure of the γ-halo ethers synthesized by us and in the correct understanding of the course of the process during the syntheses carried out by us with the γ-halo ethers.

α-Halo ethers can add to ethylenic hydrocarbons in two ways.

$$CH_2(Cl){-}OR' + CH_2{=}CH(R) \;\begin{cases} \xrightarrow{(a)} CH_2{-}CH_2{-}O{-}R' \;\; (I) \\ \qquad\quad\;\; CHCl \\ \qquad\quad\;\; R \\ \xrightarrow{(b)} CH_2{-}Cl \;\; (II) \\ \qquad\quad\;\; CH{-}CH_2{-}O{-}R' \\ \qquad\quad\;\; R \end{cases}$$

In Case (a), the halide adds to the less hydrogenated carbon (according to Markovnikov's rule); in Case (b), the halide adds to the more hydrogenated carbon (contrary to Markovnikov's rule). We studied this question by establishing the structure of the γ-halo ether obtained by the action of α-chloromethyl butyl ether on propylene. According to the scheme indicated above, two γ-halo ethers ($R{=}CH_3$, $R'{=}C_4H_9$) could be expected. In Case (a), the γ-chloro ether has a normal structure, while in Case (b), it has an iso-structure.

On substitution of hydrogen for the chlorine, from product (I) we would obtain dibutyl ether, while n-butyl isobutyl ether would be obtained from product (II). We carried out the substitution by decomposing with water the organomagnesium compound prepared from the γ-chloro ether. As a result, n-butyl ether was obtained.

Moreover, in order to establish the structure of the γ-chloro ether, we decided to prepare, by the removal of the elements of hydrogen chloride with alcoholic alkali, the corresponding unsaturated ether, in which the position of the double bond could be determined by oxidation. The unsaturated ether obtained by us from methyl γ-chlorobutyl ether by means of alcoholic alkali proved to be the methyl ether of γ-methylallyl alcohol.

The ethyl ether of γ-methylallyl alcohol was prepared from ethyl γ-chlorobutyl ether under analogous conditions. Ethoxyacetic acid, characterized by the silver salt, was isolated from the products of the oxidation of this unsaturated ether. Consequently, the γ-chloro ether obtained by us had the normal structure: $CH_3CHClCH_2CH_2{-}O{-}C_2H_5$.

The experiments provide a basis on which to assume that during the action of γ-chloro ethers on ethylenic hydrocarbons, the halide adds to the less hydrogenated carbon, and the residue ($R{-}O{-}CH_2$) adds to the more hydrogenated carbon atom (according to Markovnikov's rule).

In the synthesis of γ-halo ethers, it was necessary to start first with individual ethylenic hydrocarbons, which we obtained by dehydration of the corresponding monohydric alcohols. As the second component of the alkylation reaction, i. e., the α-halo ethers, we prepared them by the method of Lietterscheid [11] by passing hydrogen chloride or hydrogen bromide through a mixture of paraformaldehyde and the appropriate alcohol with a certain amount of cooling. In the absence of a catalyst, the α-halo ethers react almost not at all with gaseous ethylenic hydrocarbons, $ZnCl_2$ was used as the catalyst, and in the synthesis of γ-bromo ethers, $ZnBr_2$ or $ZnCl_2$ was used. In the latter case, $ZnBr_2$ acts better than $ZnCl_2$. After passing the hydrocarbon into the reaction cylinder for several minutes, the reaction mixture begins to heat, and, if not cooled, the temperature reaches 80° within a short period. With the absorption of hydrocarbon, the volume and weight of the reaction mixture increases. The transparent mixture acquires a dark red color. Cooling of the reaction mixture with ice water is necessary in order to avoid the formation of by-products. After the absorption of hydrocarbon had ceased, the reaction mixture was allowed to stand at room temperature for 4 hours. The product was then washed free of catalyst in a separatory funnel, and, after drying, was vacuum distilled. By observance of the conditions indicated above, γ-chloro esters were obtained with yields of 40-50% (based on α-chloro ether), while the yield of γ-bromo ethers was 50-70%. Constants of the γ-halo ethers synthesized are presented in Tables 1 and 2.

Halogens in positions α to the oxygen group are characterized by great lability, while those in β-positions are extremely inert [12].

During a study of the action of metallic sodium on γ-bromo-propyl ethyl ether [3], it was established that decomposition occurs with the formation of propylene and the total ether of trimethylene glycol. A review of the literature indicated that the action of metallic sodium on γ-chloro ethers has not been investigated. Our experiments showed that it does not act on γ-chloro ethers at ordinary temperatures. However, on lengthy heating of a mixture of sodium and a γ-chloro ether in anhydrous benzene at the boiling point of the solvent, partial condensation of the ether occurs with the formation of the total ether of hexamethylene glycol, $RO[CH_2]_6OR$. Moreover, the presence of allyl ether was also detected in the reaction products, formed, apparently, as a result of the splitting out of hydrogen chloride from the γ-chloro ether.

γ-Bromo ethers are more prone to react with metallic sodium than are γ-chloro ethers, and the reaction proceeds at lower temperatures. If a γ-bromo ether is added to sodium in anhydrous benzene, the reaction begins at an ordinary temperature with the liberation of heat. In the reaction mixture, in addition to the basic reaction product – the total ether of hexamethylene glycol (22%) – and a by-product – allyl ether – there is a certain amount of an ether of a monohydric alcohol ($R-CH_2-CH_2-CH_2OR$), the formation of which is the result of the partial reduction of allyl alcohol by hydrogen formed by the action of sodium on hydrogen bromide.

Metallic magnesium reacts smoothly with γ-halo ethers in absolute ether to give the Grignard reagent, which reacts with aldehydes, ketones, esters, carbon dioxide, etc. With the aid of organomagnesium compounds prepared from the γ-halo ethers, an entire series of syntheses was carried out, the results of which are the subject of a future communication.

1,3-Dihalo derivatives are formed by the action of hydrogen bromide on γ-halo ethers (80% yield). Hydrogen iodide reacts with the formation of 1, 3-dihalo derivatives (70% yield).

EXPERIMENTAL

Synthesis of γ-chlorobutyl ether. 75.0 g of α-chloromethyl butyl ether was added to a glass cylinder containing 3.5 g of freshly fused zinc chloride on glass wool. Propylene, prepared by dehydration of isopropyl alcohol, was passed through the chloro ether for a period of 36 hours. The reaction proceeded with the liberation of heat. The color of the reaction mixture was dark red. The increase in weight was 20 g. The reaction mixture was then decomposed with water, and subsequently washed with a weak solution of alkali and then with water. After drying, the product, in the amount of 69.0 g, was vacuum distilled on an oil bath. After a second distillation, 41.0 g (40%) of butyl γ-chlorobutyl ether was obtained, the constants of which are presented in Table 1 (Compound 2).

In addition, there was isolated from the reaction mixture 10.0 g of butyl alcohol, the product of the hydrolysis of the unreacted α-chloromethyl butyl ether. 12.0 g of a varnish-like, dark brown liquid, which was difficult to distil, remained in the distillation flask.

TABLE 1

α-Chloro Ethers of the Aliphatic Series •

Compound No.	Structural formula chloro ether			Name of ether	Empirical formula	Boiling point	d_{20}^{20}	n_D^{20}	MR_D		Molecular weight		% Cl	
	R	R_1	R_2						Found	Calc.	Found	Calc.	Found	Calc.
1	CH_3	H	C_2H_5	Ethyl γ-chlorobutyl	$C_6H_{13}OCl$	43—44° (15 мм); 144°	0.9357	1.4162	36.62	36.42	135.6, 140.3	136.5	25.74, 25.25	26.00
2	CH_3	H	C_4H_9	Butyl γ-chlorobutyl	$C_8H_{17}OCl$	68—69 (15 мм); 179—181	0.9146	1.4241	45.9	45.65	164.4, 165.1	164.5	21.20, 21.23	21.58
3	CH_3	H	C_5H_{11}-iso	Isoamyl γ-chlorobutyl	$C_9H_{19}OCl$	68—70 (4 мм)	0.8931	1.4204	50.62	50.27	179.7, 181.4	178.5	19.51	19.88
4	CH_3	H	C_8H_{17}	n-Octyl γ-chlorobutyl	$C_{13}H_{25}OCl$	141—144 (16 мм)	0.8959	1.438	64.61	64.12	221.7, 222.2	220.5	15.98	16.1
5	C_2H_5	H	CH_3	Methyl γ-chlorobutyl	$C_6H_{13}OCl$	92—94 (112 мм); —	0.9521	1.4224	36.46	36.41	133.1, 139.9	136.5	25.57, 25.69	26.00
6	C_2H_5	H	C_2H_5	Ethyl γ-chloroamyl	$C_7H_{15}OCl$	132—134, 161—163	0.9344	1.4250	41.18	41.03	152.6, 153.1	150.5	23.81	23.58
7	C_2H_5	H	C_4H_9	Butyl γ-chloroamyl	$C_9H_{19}OCl$	79—80 (8 мм); 190—193	0.9041	1.4273	50.72	50.27	178.2	178.5	19.39, 19.57	19.88
8	C_2H_5	H	C_8H_{17}	Octyl γ-chloroamyl	$C_{13}H_{27}OCl$	140—143 (12 мм)	0.8947	1.4402	69.11	68.74	228.2	234.5	15.12	15.14
9	CH_3	CH_3	C_2H_5	Ethyl γ-chloroisoamyl	$C_7H_{15}OCl$	91—94 (120 мм)	0.9331	1.4225	41.02	41.03	154.4, 152.4	150.5	23.27	23.58
10	CH_3	CH_3	C_4H_9	Butyl γ-chloroisoamyl	$C_9H_{19}OCl$	89—92 (18 мм)	0.9028	1.4254	50.59	50.27	174.1, 175.6	178.5	19.56	19.88
11	C_3H_7	H	C_2H_5	Ethyl γ-chlorohexyl	$C_8H_{17}OCl$	77—79 (15 мм)	0.9298	1.4362	46.27	45.65	171.2, 168.0	164.5	21.20, 21.34	21.58
12	C_3H_7-iso	H	C_5H_{11}-iso	Isoamyl γ-chloroisohexyl	$C_{11}H_{23}OCl$	113—117 (20 мм)	0.8871	1.4265	59.7	59.51	209.0	206.5	16.87	17.19
13	C_6H_{13}	H	CH_3	Methyl γ-chlorononyl	$C_{10}H_{21}OCl$	104—107 (16 мм)	0.9292	1.4434	54.96	54.89	190.0	192.5	17.97	18.44
14	C_6H_{13}	H	C_2H_5	Ethyl γ-chlorononyl	$C_{11}H_{23}OCl$	126—129 (18 мм)	0.9173	1.4452	59.93	59.51	209.7	206.55	16.96	17.19
15	C_2H_5	H	C_5H_{11}-iso	Isoamyl γ-chloroamyl	$C_{10}H_{21}OCl$	78—80 (4 мм); 204—207	0.8908	1.4230	55.03	55.89	194.3, 190.5	192.5	17.91	18.44

• Together with V. Pishnamazzade.

TABLE 2

γ-Bromo Ethers of the Aliphatic Series •

Compound No.	Structural formula of ether R—CHBr—CH_2—CH_2—O—R_1		Name of ether	Empirical formula	Boiling point	d_{20}^{20}	n_D^{20}	MR_D		Molecular weight		% Br		Yield (in %)
	R	R_1						Found	Calc.	Found	Calc.	Found	Calc.	
1	CH_3	CH_3	Methyl γ-bromobutyl	$C_5H_{11}OBr$	54.5—56° (20 мм)	1.2654	1.4491	35.40	34.69	170.7, 165.1	167	48.20	47.90	52.39
2	CH_3	C_2H_5	Ethyl γ-bromobutyl	$C_6H_{13}OBr$	68—69 (20 мм)	1.2165	1.4487	39.89	39.31	183.6, 183.2	181	43.62	44.19	55.38
3	CH_3	C_4H_9	Butyl γ-bromobutyl	$C_8H_{17}OBr$	99—100 (20 мм)	1.1400	1.4478	49.06	48.55	207.8	209	38.20	38.28	60.35
4	CH_3	C_5H_{11}-iso	Isoamyl γ-bromobutyl	$C_9H_{19}OBr$	111—112 (20 мм)	1.124	1.4476	53.07	53.16	216.1, 222.3	223	35.53	35.87	50.00
5	C_2H_5	CH_3	Methyl γ-bromoamyl	$C_6H_{13}OBr$	63—66 (21 мм)	1.2306	1.4499	39.52	39.31	178.3	181	43.66	44.19	55.20
6	C_2H_5	C_2H_5	Ethyl γ-bromoamyl	$C_7H_{15}OBr$	76.5—77 (20 мм)	1.1910	1.4489	43.92	43.93	193.1	195	40.87	41.25	71.28
7	C_2H_5	C_4H_9	Butyl γ-bromoamyl	$C_9H_{19}OBr$	110—112 (20 мм)	1.1200	1.4476	53.26	53.17	220.8	223	35.495	35.87	59.60
8	C_2H_5	C_5H_{11}-iso	Isoamyl γ-bromoamyl	$C_{10}H_{21}OBr$	110—111 (15 мм)	1.0920	1.4474	58.03	57.77	239.0	237	33.23	33.75	68.70

• Together with B. K. Zeinalovy.

Together with B. Pishnamazzade, we synthesized 15 new γ-chloro ethers, certain constants of which are presented in Table 1.

Synthesis of γ-bromodibutyl ether. γ-Bromodibutyl ether was prepared by passing propylene through a mixture consisting of 50.0 g of α-bromomethyl butyl ether (b. p. 155-157°, d_{20}^{20} 1.2710) and 2.0 g of powdered anhydrous zinc bromide. The propylene was fed over a period of 4 hours at a rate of 2 liters/hour. A total of 8 liters was fed, of which 7 liters was absorbed. During the entire course of the reaction, the reaction mixture was cooled to 10°. The weight and volume of the reaction mixture both increased with the absorption of propylene. The initially colorless reaction mixture acquired a dark green color toward the end of the reaction. At the completion of the reaction, the mixture was allowed to stand for 6 hours at room temperature. The contents of the flask, weighing 70.0 g (18 g weight increase) were then washed with water. The lower, bromo ether layer was separated from the upper, aqueous layer and then washed with a dilute solution of alkali and then with water. After drying, the product was vacuum distilled. After two successive distillations, 30.0 g (60.4%) of butyl γ-bromobutyl ether was obtained, the constants of which are presented in Table 2 (Compound 3).

Under similar conditions, 8 new γ-bromo ethers were synthesized and studied by us together with B. K. Zeinalovy; certain of their constants are presented in Table 2.

Determination of the structure of butyl γ-chlorobutyl ether. a) In order to establish the course of the addition of α-chloromethyl alkyl ethers to ethylenic hydrocarbons, the organomegnesium compound was prepared from butyl γ-chlorobutyl ether, and the resulting Grignard reagent, on decomposition with dilute acid and the usual separation, gave a substance corresponding to di-n-butyl ether [13].

B.p. 140-142°, d_{20}^{20} 0.7642, n_D^{20} 1.4002, MR_D 41.26. $C_8H_{18}O$. Calculated 40.79.

The preparation of the di-n-butyl ether indicated that the original γ-chloro ether had a normal structure.

b) In order to establish the structure of the α-chloro ethers, we decided to convert the chloro ether to an unsaturated ether in which the position of the double bond could be determined by oxidation. A mixture consisting of 30.0 g of butyl γ-chloroamyl ether (Table 1, Compound 7) and a solution of 35.0 g of KOH in 150 g of anhydrous alcohol was heated on a water bath for 8 hours. After purification and drying, the resulting product was distilled, whereby 15.0 g (60%) of the butyl ether of α-methylallyl alcohol was obtained *.

B.p. 170-174°, d_{20}^{20} 0.8083, n_D^{20} 1.4198, MR_D 44.44; calc. 44.93. Found M 137.7.
$C_9H_{18}O$. Calculated M 142.

For the oxidation of ethyl ether of γ-methylallyl alcohol, prepared by us from the corresponding γ-chloroether, 8.0 g of this ether (b. p. 99-102°; d_{20}^{20} 0.8056, n_D^{20} 1.4060) and 100 ml of distilled water were placed in a reaction flask having a side tube; then, with stirring by means of a mechanical stirrer, 20 g of potassium permanganate was introduced through the side tube of the flask while cooling the flask with ice water. Stirring was continued for an additional 3.5 hours after the addition of all of the permanganate. The resulting manganese dioxide was filtered and washed several times with hot water; the filtrate was saturated with potassium carbonate, evaporated to dryness, acidified with dilute acid, and the free organic acid was carefully extracted with ether and dried with sodium sulfate. After distillation, the resulting product was fractionated into the following fractions: 1st, 45-115°, 1.0 g; 2nd, 116-119°, 1.2 g; 3rd, 120-203°, 0.7 g; 4th, 204-209°, 1.0 g; residue, 0.5 g.

The 1st fraction had the odor of acetic acid. The 2nd fraction proved to be acetic acid (b. p. 116-118°, d_{20}^{20} 1.0492, n_D^{20} 1.3714, MR_D 12.98; calc. 12.97). The presence of acetic acid was also shown by analysis of the silver salt.

Found %: Ag 64.40, 64.36. $C_2H_3O_2Ag$. Calculated %: Ag 64.64.

On investigation, the 4th fraction proved to be ethoxyacetic acid.

B.p. 204-209°, d_{20}^{20} 1.0954, n_D^{20} 1.4198, MR_D 23.97; calc. 23.85. Found M 102.5. $C_4H_8O_3$. Calculated M 104.0

The silver salt was prepared from the acid.

Found %: Ag 50.93. $C_4H_7O_3Ag$. Calculated %: Ag 51.15.

* We, together with B. Pishnamazzade, prepared 8 new allyl ethers from the γ-chloro ethers under similar conditions.

Thus, all of the data presented above relative to the position of the double bond in the allyl ether show that γ-halomethyl alkyl ethers add to ethylenic hydrocarbons in a manner such that the halide goes to the less hydrogenated carbon and the radical ($R-O-CH_2$) goes to the more hydrogenated carbon atom.

The action of metallic sodium on methyl γ-bromobutyl ether (Table 2, Compound 1). 2.5 g of metallic sodium was covered with 34.0 g of anhydrous benzene in a round-bottom flask fitted with a reflux condenser, a mechanical stirrer, and a dropping funnel, and to this mixture was slowly added 16.7 g of methyl γ-bromobutyl ether. With the addition of the bromo ether, the surface of the sodium darkened, and a white precipitate formed. In order to prevent an increase in the temperature of the reaction mixture, the flask was periodically cooled with cold water. After the addition of the bromo ether, the reaction mixture was heated on a water bath for 3 hours with continuous stirring. After cooling, the reaction mixture was filtered from the precipitate, and the filtrate washed with water. After drying, the solvent was distilled, and the residue was vacuum distilled, giving 2 g (22.9%) of the dimethyl ether of dimethylhexanediol.

B.p. 77-80° (30 mm), d_{20}^{20} 0.8580, n_D^{20} 1.4168, MR_D 50.96; calc. 51.66. Found %: C 68.35; H 12.21. M 177.6. $C_{10}H_{12}O_2$. Calculated %: C 68.96; H 12.64. M 174.0.

Moreover, we were able to isolate methyl butyl ether from the reaction products.

B.p. 70-72°, d_{20}^{20} 0.7439, n_D^{20} 1.3719, MR_D 26.88; calc. 26.93. Found M 90. $C_5H_{12}O$. Calculated M 88.

The action of hydrogen bromide on methyl γ-bromobutyl ether.*

16.7 g of methyl γ-bromobutyl ether saturated with gaseous hydrogen bromide in the cold (−12°) was charged to a sealed tube. The tube was heated at 80° for a period of 10 hours. After cooling, the tube was opened, and the reaction product was washed with water, soda solution, and again with water. After drying, the product was vacuum distilled. A second distillation gave 18.0 g (83.3%) of 1, 3-dibromobutane.

B.p. 74-76° (22mm), d_{20}^{20} 1.7960, n_D^{20} 1.5068, MR_D 35.78; calc. 36.20. Found %: Br 73.45. M 212.1, 217.3. $C_4H_8Br_2$. Calculated %: Br 74.07. M 216.

SUMMARY

1. Conditions were worked out for the synthesis of γ-halo ethers by the alkylation of α-halo ethers with ethylenic hydrocarbons at atmospheric pressure and in the presence of anhydrous zinc chloride (up to 5% with respect to the α-halo ether).

2. 23 new γ-halo ethers were synthesized and studied.

3. It was established that in the addition of α-halo ethers to ethylenic hydrocarbons, the halide adds to the less hydrogenated carbon atom.

4. It was shown that by the action of alcoholic alkali on γ-halo ethers, the elements of hydrogen halide are split out with the formation of allyl ethers.

5. It was established that the halide in γ-halo ethers is firmly bound. Under ordinary conditions, metallic sodium does not act on γ-chloro ethers, but γ-bromo ethers undergo a Wurtz reaction.

6. 1, 3-Dihalo derivatives are formed in yields up to 80% by the action of hydrogen bromide on γ-halo ethers.

* We, together with B. K. Zeinalovy, synthesized five new 1,3-dihalo derivatives under similar conditions and studied a number of their transformations.

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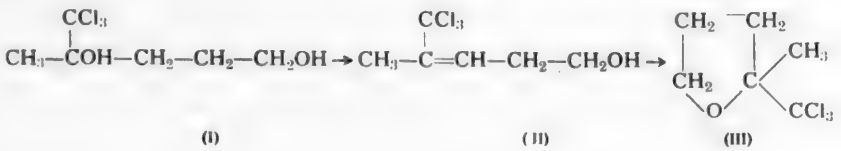
ON THE MECHANISM OF γ-GLYCOL DEHYDRATION

IV. SYNTHESIS OF 2-TRICHLOROMETHYL-2, 5-PENTANEDIOL AND INVESTIGATION OF ITS REACTION WITH SULFURIC ACID

T. A. Favorskaya and L. S. Bresler

In a preceding work [1], we showed that the tertiary alcohol methyltrichloromethylcyclopropylcarbinol, unlike other tertiary alcohols of the cyclopropane series, does not undergo the usual allylic rearrangement leading to the formation of an unsaturated primary alcohol, but is recovered unchanged from the reaction.

In this connection, it was of interest to study the course of the reaction of the corresponding γ-glycol containing a CCl_3 radical, 2-trichloromethyl-2, 5-pentanediol (I), with sulfuric acid, to investigate whether it proceeds as usual, whether the product obtained is the unsaturated primary alcohol (II) or the product of its isomerization, 2, 2-methyltrichloromethyltetrahydrofuran (III).



(I) (II) (III)

The glycol was prepared by Lombard condensation [2] of acetopropyl alcohol with chloroform in the presence of powdered potassium hydroxide in methylal solution. As is well known, the yields of product from condensations of this type are always very small; however, the yield of glycol was relatively better than the yields of the majority of monohydric alcohols prepared by this method; it was 9% while the total yield of methyltrichloromethylcyclopropylcarbinol was only 3.5% [1].

The reaction of this glycol with sulfuric acid occurred under considerably more severe conditions than those for the previously studied glycols [3-5]; even on treatment with sulfuric acid of 1:5 concentration, the glycol was recovered unchanged, and only on heating with sulfuric acid of 1:4 concentration was it converted to 2, 2-methyltrichloromethyltetrahydrofuran (III). Whether in this case the dehydration of the glycol proceeds through the intermediate formation of the unsaturated alcohol (II) or whether it proceeds by the elimination of water at the expense of the two hydroxyl groups, it is impossible to say, since it is possible that the first-formed unsaturated alcohol immediately isomerizes, under such severe conditions, to the tetrahydrofuran derivative, and therefore, cannot be detected in the reaction products.

The resulting tetrahydrofuran, although it boiled within a single-degree range, was not satisfactorily pure, since its analyses were not sufficiently good. Its oxidation with permanganate solution had to be carried out with heating, decoloration of the solution ceasing very rapidly. The neutral product isolated solidified in the condenser, and was pure 2, 2-methyltrichloromethyltetrahydrofuran.

Thus, 2, 2-methyltrichloromethyltetrahydrofuran was considerably more stable toward the action of oxidizing agents than were all of the tetrahydrofuran derivatives previously studied by us, which, although slowly, nevertheless were oxidized by permanganate solution in the cold to lactones of the corresponding hydroxy acids.

EXPERIMENTAL

Synthesis of the glycol 2-trichloromethyl-2, 5-pentanediol. The synthesis was carried out under the conditions used by Lombard and Boesch [2]. Into a round-bottom, three-neck flask, fitted with a stirrer, a low-temperature thermometer, and a dropping funnel, was placed 150 ml of anhydrous methylal; while cooling the flask with ice-salt mixture, the methylal was stirred until the thermometer indicated −15°, after which 30 g of freshly ground potassium hydroxide was introduced into the flask with vigorous stirring. When the mixture was again cooled to −15°, the dropwise introduction of chloroform (80 ml) was begun; during the introduction of the chloroform, the temperature must not rise above −5°; consequently, the addition was extended over about an hour, after which, at a temperature of −5 to −7°, 51 g of acetopropyl alcohol was added dropwise over the course of 1 hour. Stirring of the reaction mixture was continued for another 2 hours, and the mixture gradually thickened so much that the stirrer finally stopped. The contents of the flask were transferred to a beaker containing crushed ice and 200 ml of 30% sulfuric acid; the oily, lower layer was separated, the water extracted with ether, the whole dried with calcined $MgSO_4$, and the dried solution transferred to a crystallizer; on evaporation of the ether, acicular crystals of glycol gradually separated. The residue was a thick, brown, undistillable oil which did not crystallize on standing for a period of three months. 10 g of glycol was obtained, m. p. 75-76° (from petroleum ether).

Found %: Cl 47.86; OH number 2.01. M 220. $C_6H_{11}O_2Cl_3$. Calculated %: Cl 48.08; OH number 2. M 221.

Reaction of the glycol with sulfuric acid. 4 g of glycol was refluxed with 40 ml of 1:4 (46%) sulfuric acid for 6.5 hours. The aqueous solution was yellowish, and on its surface and in the condenser tube was a white, easily fusible, crystalline substance. This material was extracted in ether, and the extract was dried over sodium sulfate. The ether was distilled, and the residue was distilled under vacuum to give 2 g of a substance with the odor of camphor; it contained halogen, but did not react with CH_3MgI.

B.p. 102-103° (21 mm), n_D^{20} 1.4897, d_4^{20} 1.3352, MR_D 44.03; calc. 43.96. Found %: C 35.38; H 7.78. Cl 48.86 $C_6H_9OCl_3$. Calculated %: C 35.82; H 7.86; Cl 52.33.

The substance solidified in a freezing mixture, and precipitated in a crystalline form on pouring into water. It melted in contact with the hand. It oxidized with difficulty on heating with permanganate; after the addition of about 1/4 of the required amount of oxidizing agent to 1.5 g of the material, the color of the aqueous permanganate solution did not change in the course of several days. When oxidation was complete, the neutral product was steam distilled, extracted with ether, dried, and distilled; b. p. 92-93 ° (16 mm): the material solidified in the condenser. M. p. 25°, 0.35 g was obtained.

Found %: Cl 52.13. $C_6H_9OCl_3$. Calculated %: Cl 52.33.

We were unable to isolate any oxidation products.

SUMMARY

1. By the condensation of acetopropyl alcohol with chloroform, the glycol 2-trichloromethyl-2, 5-pentanediol was synthesized for the first time.

2. It was shown that on heating with 46% sulfuric acid, the glycol is converted to 2, 2-methyltrichloromethyltetrahydrofuran, which is not changed by heating with permanganate solution.

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A NEW SYNTHESIS OF CITRAL FROM ISOPRENE

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N. V. Kudryasheva and A. I. Pilyavskaya

Citral is one of the most important intermediate products in the synthesis of aromatic principles and vitamin A. A basic difficulty in the total synthesis of citral consists of finding readily available raw materials from which to construct its carbon skeleton.

The work of Wagner-Jauregg [1] and of A. E. Favorsky and A. I. Lebedev [2] showed that it is possible to synthesize terpene compounds by polymerization of isoprene or its derivatives (alcohols) by means of solutions of sulfuric acid in acetic acid or water. However, under these conditions a number of products are formed with carbon skeletons other than that of citral [3].

Recently, K. V. Leets [1] accomplished the synthesis of terpene chlorides, $C_{10}H_{17}Cl$, by telomerization of isoprene with its hydrochlorides (chloroisopentenes) in the presence of catalysts; the yield was 50% based on the isoprene used.

On the basis of this method, we developed a new method for the synthesis of citral according to the following scheme:

$$C_5H_8 + HCl \begin{cases} \rightarrow (CH_3)_2CCl{-}CH{=}CH_2 \\ \rightarrow (CH_3)_2C{=}CH{-}CH_2Cl \end{cases} \xrightarrow[SnCl_4]{+\,C_5H_8}$$

$$\rightarrow (CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CH_2Cl \xrightarrow{+\ \text{urotropine}}$$

$$\rightarrow [C_{10}H_{17} \cdot C_6H_{12}N_4]^+Cl^- \xrightarrow[H_2O]{+\,CH_2O}$$

$$\rightarrow (CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CHO$$

The conversion of geranyl chloride, which is present in the mixture of terpene chlorides, into citral was carried out by the method of Sommelet [5] using certain new conditions such as, for example, the introduction of excess formaldehyde into the reaction mixture [6, 7]. The use of the pure, crystalline compound of geranyl chloride with urotropine permitted preparation of citral with a yield of 78% of theoretical. Saponification of the remaining terpene chlorides, which did not react with urotropine, gave only α-terpineol with a m. p. of 33°.

Thus, it was established that the mixture of terpene chlorides obtained as described above consisted basically of geranyl chloride and terpinyl chloride. It follows from this that the addition of isoprene hydrochlorides to isoprene proceeds with the formation of a carbon skeleton corresponding to that of citral. The formation of terpinyl chloride can be considered as a process of the cyclization of geranyl chloride.

EXPERIMENTAL

1. Preparation of terpene chlorides from isoprene. Isoprene was hydrochlorinated with hydrogen chloride under conditions described by Ultee [8]. After absorption of 70 g of hydrogen chloride by the isoprene (400 g), there was obtained 470 g of a mixture of isoprene and its hydrochlorides. The content of hydrochlorides (according to chlorine analysis) was 43.5%. The mixture (470 g) was then diluted with methylene chloride (767 g), and a

solution of 1 g of stannic chloride in 32 g of methylene chloride was added while stirring and cooling. After two minutes, the reaction was stopped short by the addition of 20 g of urea. The solution of telomers was filtered from the precipitate, and distilled to remove the solvent and residual unreacted starting material (1118 g). 98 g of reaction product with a content of 18.5% bound HCl (corresponding to 80 g of isoprene) was obtained, and after distillation under vacuum, there was obtained 50.5 g of a terpene chloride fraction (50% of the isoprene used).

B. p. 60-85° (2 mm), d_4^{20} 0.912-0.960, n_D^{20} 1.474-1.481. Found %: Cl 20.45. $C_{10}H_{17}Cl$. Calculated %: Cl 20.53.

2. Preparation of the crystalline compound of geranyl chloride with urotropine. The terpene chlorides (41.5 g) were dissolved in 200 ml of anhydrous acetone, 17 g of urotropine was added, and the mixture was stirred at room temperature (18-20°) for 3 days. The precipitated salt of the quaternary base was separated by filtration, washed with acetone, and dried under vacuum. The yield was 31.6 g.

Found %: Cl 11.32. $C_{10}H_{17}$. $C_6H_{12}N_4Cl$. Calculated %: Cl 11.33.

3. Preparation of citral. The salt of the quaternary base (30 g) was dissolved in 1.2 liters of water, 20 g of formalin (30%) was added, and the reaction mixture was heated at the boiling point for 30 minutes. The resulting aldehyde was separated by steam distillation. The aldehyde was extracted with toluene, the extract was washed and dried, and the content of $C_{10}H_{16}O$ aldehyde was determined as 11.3 g (78%, with hydroxylamine hydrochloride). Distillation under vacuum gave 10 g of citral (aldehyde content 99%).

B.p. 65-70° (1 mm), d_4^{20} 0.8919, n_D^{20} 1.4890.
Literature data [9]: Citral a, b.p. 118-119° (20 mm), d_4^{20} 0.8898, n_D^{20} 1.4891; Citral b, b.p. 117-118° (20 mm) d_4^{20} 0.8888, n_D^{20} 1.4891.

Pseudoionone and ionone were prepared from the citral by well-known methods [10, 11].

Pseudoionone: B.p. 125-126° (4 mm), d_4^{20} 0.8975, n_D^{20} 1.5310
Literature data [12]: B.p. 143-145° (12 mm), d_4^{20} 0.8973, n_D^{20} 1.5312.
Ionone: B.p. 105-110° (5 mm), d_4^{20} 0.9332, n_D^{20} 1.5006.
Literature data [13]: α-ionone, B.p. 121-122° (10 mm), d_4^{20} 0.9319, n_D^{20} 1.4982; β-ionone b.p. 128-129° (10 mm), d_4^{20} 0.9448, n_D^{20} 1.5195-1.5200.

Preparation of terpineol. In order to completely eliminate the geranyl chloride, the acetone filtrate containing the residual chlorides (see paragraph 2) was heated with 10 g of urotropine on a water bath for 2 hours. The precipitated crystals were filtered, the acetone distilled from the mother liquor, the residue washed free from traces of urotropine, and the resulting chloride (18 g) was hydrolyzed in an aqueous-alcoholic solution (3:1) of $Pb(NO_3)_2$ (5 g) with excess $PbCO_3$ (20 g) by refluxing for 3 hours. The solution was then diluted with water (5:1), and the supernatant oil extracted with toluene. The resulting alcohols were bound in the form of the borate esters by reaction with butyl borate, all impurities were eliminated by distillation with excess butyl borate [14], and, after decomposition of the borate esters and distillation, a terpene alcohol (8 g) was obtained, which crystallized on the introduction of a crystal of pure terpineol and which, possessing the appropriate constants, was D, L- α-terpineol. M.p. 33°; a mixture with a known sample [12] showed no depression of the melting point.

B.p. 87.5° (6 mm), d_4^{20} 0.927, n_D^{20} 1.4805; bromine number 108.7.

SUMMARY

1. A new synthesis of citral from isoprene through geranyl chloride was carried out.

2. It was shown that telomerization of isoprene with its hydrochlorides under the catalytic influence of $SnCl_4$ gives terpene chlorides consisting chiefly of geranyl chloride and terpinyl chloride.

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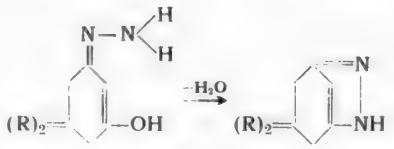
INVESTIGATIONS IN THE FIELD OF POLYMETHYLENE RINGS

XXVI. REACTIONS AND REACTION PRODUCTS OF 1, 3-CYCLOHEXANEDIONE, DIMEDONE, AND ACETYLACETONE WITH HYDRAZINE AND DIMETHYLHYDRAZINE

N. A. Domnin, Van Syui-kun and N. S. Glebovskaya

We have previously investigated the reaction of cyclopentanedione and cyclohexanedione with hydrazine and dimethylhydrazine [1], and it was shown that cyclic 1, 3-diketones occupy a special place in such reactions, differing from cyclic 1, 2- and 1, 4-diketones. In connection with these investigations, it seemed of interest to study the reactions of aliphatic 1, 3-diketones with hydrazine and dimethylhydrazine under the same conditions. 2, 4-Pentanedione (acetylacetone) was selected for this investigation.

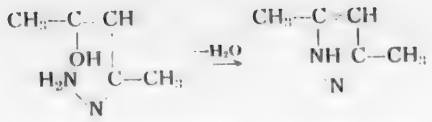
Along this line, we showed that the similarly structured 1, 3-cyclohexanedione and 5, 5-dimethyl-1, 3-cyclohexanedione, on the one hand, and acetylacetone, on the other, behave differently in their reactions with hydrazine and dimethylhydrazine. 1, 3-Cyclohexaneidione and dimedone do not form monohydrazones, while acetylacetone does. Acetylacetone readily forms both the monodimethylhydrazone and the bisdimethylhydrazone, while both 1, 3-cyclohexanedione and dimedone form only the monodimethylhydrazone, and do not form bis-dimethylhydrazones at all. These facts can be explained on the basis of concepts developed by us previously [1]. It is possible to give these facts, which we have established, another interpretation. If we assume complete analogy in the courses of the reactions of 1, 3-cyclohexanedione, dimedone, and acetylacetone with hydrazine and dimethylhydrazine, the following explanation may be proposed. 1, 3-cyclohexanedione and dimedone, being enolized, react, as does acetylacetone, with 1 molecule of hydrazine, and the resulting monohydrazone cyclizes, with the elimination of water, into pyrazole derivatives



It is quite evident that such bicyclic molecules are incapable of existence, and will either isomerize into stable molecules or convert to polymeric products.

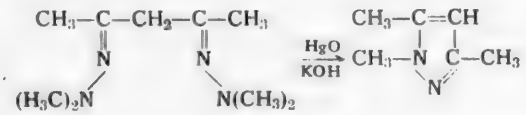
Considering the monodimethylhydrazones of 1, 3-cyclohexanedione and dimedone from this point of view, it can be predicted that they will be unstable, as is confirmed experimentally. However, it is still not clear why these two ketones are incapable of forming bisdimethylhydrazones.

The correctness of our views on the formation of five and six-membered rings and the emergence of steric hindrance in them owing to the various substituents is confirmed by the facts obtained in the present work. Thus, the monohydrazone of acetylacetone, prepared and characterized for the first time, proved to be unstable, and during recrystallization, long standing, or in the presence of hydrazine it was converted into 3, 5-dimethylpyrazole.



Attempts to prepare the dihydrazone of acetylacetone were unsuccessful. Evidently, before the acetylacetone enters into reaction with the second molecule of hydrazine, the already formed monohydrazone is converted by the elimination of water into a more stable product – 3, 5-dimethylpyrazole. We were also unable to isolate mono- and hydrazones in the case of dimethyl- and methylethylacetylacetones. These facts confirm that the formation of pyrazoles from aliphatic 1, 3-diketones proceeds through the temporary emergence of unstable intermediate products – monohydrazones. If the active hydrogen atoms in the $N-NH_2$ group of hydrazine are replaced by methyl radicals, then acetylacetone readily reacts with unsymmetrical dimethylhydrazine to form the stable monodimethylhydrazone and bisdimethylhydrazone. The latter was first prepared and characterized by us.

We should note here an interesting fact established by us. It is well known that Wolff-Kishner oxidative decomposition is undergone only by hydrazine derivatives. Quite by chance and in another connection, we observed that our bisdimethylhydrazone of acetylacetone undergoes oxidative decomposition with mercuric oxide and potassium hydroxide to give 1, 3, 5-trimethylpyrazole.



The decomposition was carried out under various conditions, and proceeded with considerable, but incomplete, liberation of nitrogen giving as the decomposition product in all cases 1, 3, 5-trimethylpyrazole.

This new reaction has not been described in the literature, but it is of great interest. We are able to offer nothing specific regarding its mechanism, since further investigation and the accumulation of new facts are required for an understanding of the mechanism. With this aim, we attempted to prepare the monodimethylhydrazone of methylethylacetonylcarbinol starting with methylethylacetonylcarbinol synthesized by us; however, the latter did not react with dimethylhydrazine.

Finally, we established that 3, 5-dimethylpyrazole is formed by the action of hydrazine on the monodimethylhydrazone of acetylacetone. It is probable that the hydrazine expels the dimethylhydrazine group to give the monohydrazone, which closes the pyrazole ring by the elimination of water.

EXPERIMENTAL

Monohydrazone hydrate of acetylacetone. A solution of 1 g of acetylacetone in 10 ml of anhydrous ethyl alcohol was added dropwise, while stirring vigorously and cooling with ice water, to a solution of 2 g of hydrazine hydrate in 20 ml of anhydrous alcohol. The resulting white precipitate was filtered, washed with cold anhydrous alcohol, and dried in a vacuum desiccator for 12 hours. 0.8 g (70%) of a material with a m. p. of 59.5-60.5° was obtained.

Found %: N 21.06, 21.49. M 125, 135. $C_5H_{12}O_2N_2$. Calculated %: N 21.21. M 132.

During recrystallization, upon the action of hydrazine hydrate, and during long standing, the monohydrazone hydrate was converted to 3, 5-dimethylpyrazole. M.p. 106-108° A mixture with a known sample of 3, 5-dimethylpyrazole showed no m. p. depression.

Found %: C 61.89, 62.05; H 8.33 8.30; N 29.38, 29.45. $C_5H_8N_2$. Calculated %: C 62.10, H 8.33, N 29.56.

Monodimethylhydrazone of acetylacetone. 20 g of freshly distilled dimethylhydrazine was added dropwise, while stirring and cooling with ice water, to 29.2 g of acetylacetone. The reaction proceeded with the liberation of heat. Upon distillation, there was obtained 34 g (83%) of product in the form of an oily liquid with a yellow color and a disagreeable odor.

B.p. 74-75° (8.5 mm), d_4^{20} 0.9581, n_D^{20} 1.4930, MR 43.05; calc. 42.20 Found %: N 19.31, 19.36. $C_7H_{14}ON_2$. Calculated %: N 19.72.

Bisdimethylhydrazone of acetylacetone. 40 g of acetylacetone was added dropwise, while stirring and cooling with ice water, to 60 g of freshly distilled dimethylhydrazine (slight excess). After two distillations, there was obtained 56 g (77%) of product in the form of an oily liquid with a yellow color and a disagreeable odor.

B.p. 75-76° (6 mm), d_4^{20} 0.9144, n_D^{20} 1.4810, MR 57.20, calc. 56.99. Found %: N 30.28, 30.21. $C_9H_{20}N_4$. Calculated %: N 30.43.

Decomposition of acetylacetone bisdimethylhydrazone. 106 g of mercuric oxide, 0.5 g KOH, and 300 ml of anhydrous alcohol were placed in a flask fitted with a mercury seal, a stirrer, and a reflux condenser. After the mixture had been heated to the boiling point of the alcohol, 30 g of acetylacetone bisdimethylhydrazone was added dropwise. The mercuric oxide gradually changed color to black. Heating was continued for 5 hours, until the evolution of nitrogen was complete. After cooling the reaction mixture to room temperature, the precipitate was filtered. The alcoholic solution was diluted with water and extracted with ether to free it from tar. The ethereal solution was dried over sodium sulfate. After elimination of the ether, the residue was distilled under vacuum. During the distillation, a fraction boiling at 64° (10 mm) was collected; this fraction immediately crystallized. M. p. 35-37°. A mixture with a known sample of 1, 3, 5-trimethylpyrazole showed no melting point depression. The yield was 11%.

The yield of 1, 3, 5-trimethylpyrazole is increased to 20% and higher if the decomposition is carried out in carbon tetrachloride solution and in an atmosphere of nitrogen.

Found %: C 64.98: H 9.29; N 25.66 M 106, 108. $C_6H_{10}N_2$. Calculated %: C 65.45; H 9.09; N 25.67. M 110.

The action of potassium hydroxide and mercuric oxide on acetylacetone monodimethylhydrazone. Heating an alcoholic solution of the monodimethylhydrazone with potassium hydroxide under the conditions used for the decomposition of the bisdimethylhydrazone resulted in the formation of tar. By distillation of the tar, we were able to separate a small amount of acetylacetone, which was characterized by its 2, 4-dinitrophenylhydrazone.

Found %: N 24.26, 24.00. $C_{11}N_{12}O_5N_4$. Calculated %: N 24.03.

The action of hydrazine hydrate on acetylacetone monodimethylhydrazone. Heat was evolved when 2 g of acetylacetone monodimethylhydrazone was mixed with 2 g of hydrazine hydrate. The reaction mixture was heated for an additional hour at 150°. On cooling, a white crystalline precipitate formed, which, after recrystallization from benzene, melted at 106-108°. A mixture with a known sample of 3, 5-dimethylpyrazole showed no melting point depression.

Found %: N 28.60, 28.82. $C_5H_8N_2$. Calculated %: N 28.74.

Methylethylacetonylcarbinol was prepared by organomagnesium synthesis. 48.6 g of magnesium, 218 g of ethyl bromide, and 158 g of acetylacetone were used in the reaction. 166 ml of 37% hydrochloric acid, which was diluted with two volumes of water, was used for the decomposition of the organomagnesium complex. Distillation of the reaction product showed that it consisted chiefly of unreacted acetylacetone and 2-ethyl-4-pentanone. Repeated distillations gave 10 g (5%) of methylethylacetonylcarbinol.

B.p. 100-107° (7 mm), d_4^{20} 0.9546, n_D^{20} 1.4612, MR 37.11; calc. 37.37 Found %: OH 12.99. $C_7H_{14}O_2$. Calculated %: OH 13.08 (Terentyev method).

The methylethylacetonylcarbinol did not react with dimethylhydrazine.

SUMMARY

1. The monohydrazone hydrate and the mono- and bisdimethylhydrazones of acetylacetone and methylacetonylcarbinol were prepared and characterized for the first time.

2. A stereochemical explanation is presented for the different behavior of 1, 3-cyclohexanedione, dimedone, and acetylacetone with hydrazine and dimethylhydrazine.

3. It was shown that oxidative decomposition of acetylacetone bisdimethylhydrazone with mercuric oxide gives 1, 3, 5-trimethylpyrazole.

4. It was established that the action of hydrazine hydrate on acetylacetone monodimethylhydrazone yields 3, 5-dimethylpyrazole.

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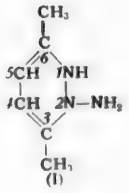
INVESTIGATIONS IN THE FIELD OF POLYMETHYLENE RINGS

XXVII. REACTIONS AND REACTION PRODUCTS OF 1, 4-CYCLOHEXANEDIONE AND ACETONYLACETONE WITH HYDRAZINE AND DIMETHYLHYDRAZINE

N. A. Domnin, M. N. Zelenina and N. S. Glebovskaya

We have shown that 1, 4-cyclohexanedione readily reacts with hydrazine and dimethylhydrazine to give the corresponding dihydrazones and bisdimethylhydrazones [1].

For comparison, it seemed to us to be of interest to investigate the manner in which analogous 1, 4-diketones with an open chain would react with hydrazine and dimethylhydrazine under the same conditions. With this aim, we investigated the reaction of acetonylacetone with hydrazine and dimethylhydrazine.



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Experimental data obtained by us showed that the monohydrazone and dihydrazone are not obtained in any amount by the reaction of acetonylacetone with hydrazine; rather, the final product is 2-amino-3, 6-dimethyldihydropyridazine (I). From this fact, it can be concluded that, in the first place, the carbonyl groups of acetonylacetone react with hydrazine at the same rate. In the second place, the resulting dihydrazone is unstable under reaction conditions, and, liberating ammonia, cyclizes into a stable six-membered heterocyclic ring. In the third place, closure of the ring is due to the lability of the hydrogen atoms in the $=N-NH_2$ of $-NH-NH_2$ group. From the latter conclusion it follows that cyclization of the dihydrazone of acetonylacetone will not occur if the two hydrogens in the $-NH_2$ group of hydrazine are replaced by radicals, methyl radicals, for example. We showed experimentally the correctness of this conclusion by reacting acetonylacetone with dimethylhydrazine; from this reaction we obtained, and characterized, the bisdimethylhydrazone, which was formed in 80% yield and underwent no further conversions.

Comparison of the reactions of acetonylacetone and 1, 4-cyclohexanedione with hydrazine is of particular interest. In the dihydrazones of 1, 4-cyclohexanedione and the aliphatic 1, 4-diketone (acetonylacetone), there are two groups $-=N-NH_2$ or $-NH-NH_2$, which are completely equivalent in their chemical properties and which occupy 1, 4-positions in both dihydrazones. In addition to this, between the two dihydrazones there is a large difference in their steric structures. In 1, 4-cyclohexanedione, both $=N-NH_2$ or $-N-NH_2$, groups are on opposite ends of the six-membered ring, spatially separated and, owing to the very limited free rotation, more or less sterically fixed. Therefore, they are incapable of reacting with each other – incapable of liberating a molecule of ammonia with the closure of a six- or seven-membered ring. Moreover, if such a bicyclic system were to emerge, the valence angles would be greatly distorted with double bonds at the junction of carbon atoms and, according to Bredt's rule, would be incapable of existence. On the other hand, in the dihydrazone of acetonylacetone, owing to the great range of free rotation, the reactive $=N-NH_2$ or $-NH-NH_2$ groups are not strictly fixed in space, and can approach each other, liberating ammonia and thereby closing a six-membered ring, so that the product of the reaction of acetonylacetone with hydrazine is 2-amino-3, 6-dimethyldihydropyridazine.

The considerations regarding steric hindrance presented here not only satisfactorily explain the established facts, but also make it possible to raise new questions and to plan routes for their experimental solution.

Thus, from the ideas presented, it is possible to come to the conclusion that the reaction of 1, 4-cyclohexanedione and of acetonylacetone with dimethylhydrazine should give equally stable bisdimethylhydrazones. The correctness of this conclusion was experimentally confirmed: we obtained and characterized the bisdimethylhydrazones of 1, 4-cyclohexanedione and of acetonylacetone.

EXPERIMENTAL

With some changes, acetonylacetone was prepared by the method of Nef [2] and Knorr [3]. Diacetylsuccinic ester was prepared and recrystallized from 50% acetic acid. M. p. 89-90°. Yield, 50%. Over the course of an hour, 100 parts of the diacetylsuccinic ester was dissolved in 600 parts of 20% aqueous potassium carbonate, and the solution was refluxed for 3-4 hours. From the resulting transparent, yellow liquid, acetonylacetone was separated by the addition of 100 parts of potassium carbonate. The yield was 70%. B.p. 190-195.5°, 89° (25 mm), n_D^{20} 1.4441.

2-Amino-3, 6-dimethyldihydropyridazine (product of the reaction of acetonylacetone with 2 molecules of hydrazine hydrate). Into a flask, fitted with a mechanical stirrer, was placed hydrazine hydrate (2 moles); the flask was cooled with water. With continuous stirring, the acetonylacetone was added through a dropping funnel. Turbidity immediately began to appear in the solution. Toward the end of the reaction, the reaction mixture solidified in the form of fine, white crystals, which were dried on a porous plate and recrystallized from ethyl alcohol. The substance was difficultly soluble in water, benzene, ether, and dioxane and readily soluble in methyl and ethyl alcohols. The yield was 90-95%. On standing, the crystals became yellow and deliquesced, forming a brown liquid.

Material obtained from different experiments did not have the same melting point. Crystals with melting points of 90-110° and 128-130° were obtained. The substance having these different melting points had the same molecular weight and the same percentage contents of carbon, hydrogen, and nitrogen. Recrystallization changed the melting point very little. Thus, the substance with a m. p. of 87-110° had a m. p. of 90-110° after the third recrystallization. Crystals with a m. p. of 90-110° were allowed to stand for a week, and were then recrystallized from alcohol; they then had a m. p. of 128-129° and 128-130°.

Substance with a m.p. of 128-130°. Found %: C 57.52, 57.54; H 8.88, 9.15; N 33.79, 33.62. M 123 (Rast) $C_6H_{11}N_3$. Calculated %: C 57.57, H 8.85; N 33.57 M 125.1.
Substance with a m.p. of 90-110°. Found %: N 33.55, 33.51. M 126.9 $C_6H_{11}N_3$. Calculated %: N 33.57. M 125.1.

Synthesis of acetonylacetone bisdimethylhydrazone. 5.3 g (2 moles) of dimethylhydrazine was placed in a round-bottom flask fitted with a mechanical stirrer. 5 g (1 mole) of acetonylacetone was introduced into the flask through a dropping funnel while stirring. The reaction was carried out at room temperature, and proceeded without the liberation of heat. 5 g (80%) of the bisdimethylhydrazone was obtained. Acetonylacetone bisdimethylhydrazone is a colorless liquid which darkens on standing in air.

B. p. 87-90° (5 mm), 104–105° (15 mm), d_4^{20} 0.8919, n_D^{20} 1.4680, MR 61.81; calc. 61.78. Found %: N 28.40, 28.35. M 192.2. $C_{10}H_{22}N_4$. Calculated %: N 28.27. M 198.

SUMMARY

1. It was established that the reaction of hydrazine with 1, 4-cyclohexanedione gives the dihydrazone, and that with acetonylacetone gives 2-amino-3, 6-dimethyldihydropyridazine.

2. The reaction of dimethylhydrazine with 1, 4-cyclohexanedione and with acetonylacetone gives the bisdimethylhydrazones.

3. These facts are explained in the light of the stereochemistry of a six-membered ring and steric hindrance.

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Leningrad State University

SYNTHESIS OF DIETHYLAMINOMETHYL ETHERS OF DIMETHYLETHYNYLCARBINOL, DIMETHYLVINYLETHYNYLCARBINOL AND TETRAMETHYLBUTYNEDIOL

E. S. Lagucheva

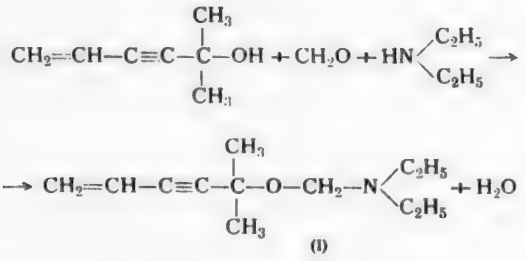
It has previously been shown that β-cyanoethyl and β-cyanoethoxyethyl ethers of dimethylethynylcarbinol enter smoothly into the Mannich reaction, yielding the corresponding aminomethylation products [1, 2].

The aim of the present work was an investigation of the behavior of acetylenic alcohols themselves in aminomethylation reactions. This was the more interesting since, in the only work devoted to this question [3], the attempted aminomethylation of the indicated alcohols was unsuccessful, while the aminomethylation of the acetates of these alcohols proceeded with good yields of the aminomethyl derivatives. The authors [3] explained this result by the negative effect of the hydroxyl group of acetylenic α-carbinols on the course of the aminomethylation reaction at the acetylenic hydrogen. As regards the possibility of aminomethylation at the hydrogen of a tertiary hydroxyl, this question is not touched upon in the cited article.

As the present work showed, tertiary acetylenic alcohols are readily aminomethylated with the formation of the corresponding dialkylaminomethylalkyl ethers. As a result of this reaction, we obtained the aminomethylation products of dimethylethynylcarbinol, dimethylvinylethynylcarbinol, and tetramethylbutynediol. In addition to these products, the aminomethylation products of the β-hydroxyethyl ether of dimethylethynylcarbinol and the β-hydroxyethyl ether of dimethylvinylethynylcarbinol were also synthesized.

Paraformaldehyde and diethylamine were used as the aminomethylating agents. The reaction was carried out at the boiling point of the mixture in organic solvents—dioxane or benzene [4].

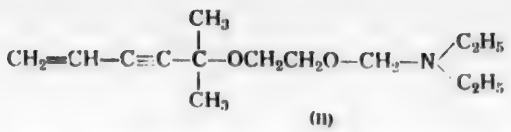
Aminomethylation of dimethylvinylethynylcarbinol in dioxane medium gave its diethylaminomethyl ether (I).



(I)

By carrying out the aminomethylation of dimethylvinylethynylcarbinol in benzene medium, the benzene vapors removing the water from the sphere of the reaction, we were able to increase the yield of diethylaminomethyl ether of dimethylvinylethynylcarbinol (from 27.7 to 71.8%).

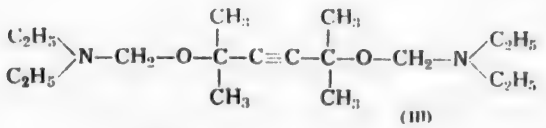
By aminomethylation of the β-hydroxyethyl ether of dimethylvinylethynylcarbinol in benzene medium, we obtained the β-diethylaminomethoxyethyl ether of dimethylvinylethynylcarbinol (II).



(II)

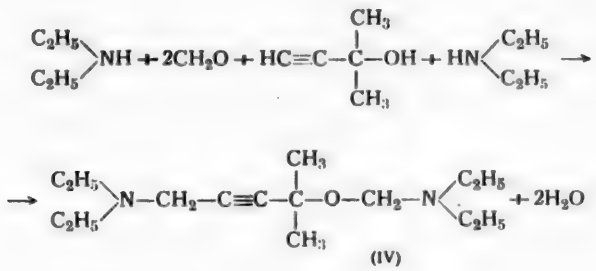
The comparatively low yield of this product (43.5%) is explained by the formation of tar from part of it during fractionation as a result of polymerization.

Aminomethylation of tetramethylbutynediol was also carried out in benzene medium; this gave the bis-diethylaminomethyl ether of tetramethylbutynediol (III) (63.4%).



(III)

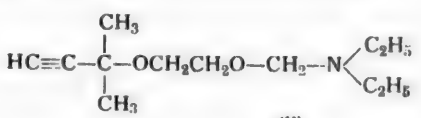
The aminomethylation of dimethylethynylcarbinol in benzene medium gave two products—the diethylaminomethyl ether of 1-diethylamino-4-methyl-2-pentyn-4-ol (IV) (in very small amount) and, chiefly, tetraethyldiaminomethane, which was formed from the diethylamine and formaldehyde.



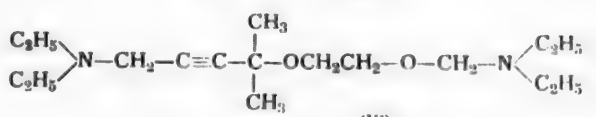
(IV)

Such a course of the reaction is evidently explained by the tendency toward hydrolysis of the amino ether of dimethylethynylcarbinol (IV) [5, 6] and by the greater stability under the reaction conditions of tetraethyldiaminomethane [5, 7].

On aminomethylation in benzene medium, the β-hydroxyethyl ether of dimethylethynylcarbinol gave the product of its aminomethylation at the hydroxyl group—β-diethylaminomethoxyethyl ether of dimethylethynylcarbinol (V) (58.7%). Along with this was formed a small amount of the β-diethylaminomethoxyethyl ether of 1-diethylamino-4-methyl-2-pentyn -4-ol (VI) by the reaction of two molecules of formaldehyde and two molecules of amine with the β-hydroxyethyl ether of dimethylethynylcarbinol.



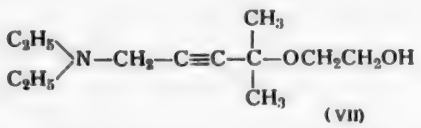
(V)



(VI)

The structure of the β-diethylaminomethoxyethyl ether of dimethylethynylcarbinol (V) was confirmed by analysis for nitrogen content and by qualitative reaction for free acetylenic hydrogen, and that of the β-diethylaminomethoxyethyl ether of 1-diethylamino-4-methyl-2-pentyn-4-ol (VI) by analysis for nitrogen content and by its failure to give a qualitative reaction for acetylenic hydrogen.

In addition, we attempted the aminomethylation of the β-hydroxyethyl ether of dimethylethynylcarbinol at the acetylenic hydrogen. Carrying out the reaction in dioxane, instead of the expected product – the β-hydroxyethyl ether of 1-diethylamino-4-methyl-2-pentyn-4-ol (VII) – we obtained the β-diethylaminomethoxyethyl ether of 1-diethylamino-4-methyl-2-pentyn-4-ol (VI) (55.37%).



(VII)

The formation of this amino ether (VI) indicates that it is quite stable, and does not hydrolyze under reaction conditions. This is evidently explained by the rather higher molecular weight of this ether.

From the results of the aminomethylation of the β-hydroxyethyl ether of dimethylethynylcarbinol, it is seen that aminomethylation at an acetylenic hydrogen in benzene medium, i. e., with the removal of water from the sphere of the reaction, proceeds to a very slight extent. This phenomenon was also observed by us during aminomethylation of the β-cyanoethyl ether of dimethylethynylcarbinol.

Thus, when this process was carried out in benzene medium with removal of reaction water, the β-cyanoethyl ether of 1-diethylamino-4-methyl-2-pentyn-4-ol was obtained with a yield of only 28.3%. Moreover, there was obtained a certain amount of a by-product of the reaction – tetraethyldiaminomethane – and 53.5% of the original β-cyanoethyl ether of dimethylethynylcarbinol was recovered from the reaction.

On the contrary, when the reaction is carried out in dioxane medium, the yield of the β-cyanoethyl ether of 1-diethylamino-4-methyl-2-pentyn-4-ol comprised 75.4% [1].

EXPERIMENTAL

1. Preparation of the diethylaminomethyl ether of dimethylvinylethynylcarbinol (I). a) In dioxane medium. Into a flask, fitted with a stirrer and a reflux condenser, was placed 55 g of dimethylvinylethynylcarbinol, 40.15 g of diethylamine, 18 g of paraformaldehyde, and 30 ml of dioxane. The reaction was carried out at the boiling point of the mixture for a period of 6 hours.

At the conclusion of the reaction, the excess paraformaldehyde was washed out with water, the product extracted with ether and the ether layer separated from the water layer. The solvent was then distilled under a slight vacuum, and the residue was fractionated under vacuum. First, the unreacted carbinol fraction, boiling in the range 54-55° (10 mm), 25.5 g, n_D^{20} 1.4768, was distilled in a column (of the type described in the paper of Kazansky and co-workers [8], with a Whitmore-Lux condenser and Fenske packing). The product was distilled from a Claisen flask. From this distillation was obtained 27 g (27.7%) of the diethylaminomethyl ether of dimethylvinylethynylcarbinol in the form of a lightly colored, mobile liquid.

B.p. 88-90° (10.5 mm), n_D^{20} 1.4599; d_{20}^{20} 0.8650; MR_D 61.33; calc. 60.73. Found %: N 7.64. $C_{12}H_{21}ON$. Calculated %: N 7.18.

b) In benzene medium. In distinction to the preceding experiment, the reaction was carried out in benzene (75 ml) with removal of the water formed in the course of the reaction by the benzene vapors. The amounts of the components and the ratios between them were the same as in the preceding experiment. The reaction was carried out over a 5.5-hour period at the boiling point of the mixture (80-97°). On completion of the reaction, the reaction mixture was subjected to the usual treatment and to distillation. During the fractionation, 70 g (71.8% of theoretical or 85.90% calculated on the carbinol reacted) of the diethylaminomethyl ether of dimethylvinylethynylcarbinol, boiling in the range 88-90° (10 mm), was collected.

B.p. 88-90° (10 mm), d_{20}^{20} 0.8653; n_D^{20} 1.4602, MR_D 61.60; calc. 60.73. Found %: N 7.19, 7.28. $C_{12}H_{21}ON$. Calculated %: N 7.18

2. Preparation of the β-diethylaminomethoxyethyl ether of dimethylvinylethynylcarbinol (II). The ether was prepared by the reaction of 30.8 g of the β-hydroxyethyl ether of dimethylvinylethynylcarbinol with 14.6 g of diethylamine and 6 g of paraformaldehyde in a medium of 75 ml of benzene.

18 g (43.5%) of the β-diethylaminomethoxyethyl ether of dimethylvinylethynylcarbinol, in the form of a colorless, mobile liquid, was obtained from the reaction mixture by fractionation. (Part of the product, 7 g, polymerized in the kettle).

B.p. 95-97° (2 mm), d_{20}^{20} 0.9200, n_D^{20} 1.4634, MR_D 71.70; calc. 71.63. Found %: N 5.83, 5.85. $C_{14}H_{25}O_2N$. Calculated %: N 5.86.

3. Preparation of the bisdiethylaminomethyl ether of tetramethylbutyndiol (III). The ether was prepared by heating 71 g of tetramethylbutyndiol, 110 g of diethylamine, and 45 g of paraformaldehyde in a medium of 100 ml of benzene. The process was carried out over a period of 5 hours at the boiling point of the mixture (80-105°) and with constant removal of the water formed during the reaction (by benzene vapors). By the usual treatment of the reaction mixture (Experiment 1), 99 g (63.46%) of the bisdiethylaminomethyl ether of tetramethylbutyndiol (III) was separated in the form of a lightly colored, mobile liquid.

B.p. 125-129° (7 mm), d_{20}^{20} 0.8844, n_D^{20} 1.4480, MR_D 94.52; calc. 94.49 Found %: C 68.88, 68.80; H 11.99, 12.0; N 9.21, 9.10. $C_{18}H_{36}O_2N_2$. Calculated %: C 69.23; H 11.54; N 8.97.

4. Diethylaminomethyl ether of 1-diethylamino-4-methyl-2-pentyn-4-ol (IV). 42 g of dimethylethynylcarbinol, 80.3 g of diethylamine, 23 g of paraformaldehyde, and 100 ml of benzene were heated at 78-95° for 6 hours. The water formed during the reaction was removed by benzene vapors. On completion of the process and after the appropriate treatment (Experiment 1), the reaction mixture was subjected to fractionation; this gave two fractions.

The 1st fraction, 26.5 g, proved to be tetraethyldiaminomethane [5, 7].

B.p. 61-63° (18 mm), 163-164.5° (757 mm), d_{20}^{20} 0.7993, n_D^{20} 1.4269 Found %: C 68.20; H 14.08; N 16.48, 16.13. $C_9H_{22}N_2$. Calculated %: C 68.35; H 13.92; N 17.70.

The 2nd fraction, b. p. 138-139° (6 mm), 1.2 g, was the diethylaminomethyl ether of 1-diethylamino-4-methyl-2-pentyn-4-ol (IV), and was a yellow, glycerin-like liquid; n_D^{20} 1.4631.

Found %: N 11.05, 11.23 $C_{15}H_{30}ON_2$. Calculated %: N 11.02.

5. Aminomethylation of the β-hydroxyethly ether of dimethylethynylcarbinol. a) In benzene medium. The β-diethylaminomethoxyethyl ether of dimethylethynylcarbinol (V) was prepared by heating 25.6 g of the β-hydroxyethyl ether of dimethylethynylcarbinol, 32.12 g of diethylamine, and 14.4 of paraformaldehyde in a medium of 75 ml of benzene. The process was carried out by simmering for about 2 hours without distillation of water; the temperature was then increased, and the water was removed from the sphere of the reaction by benzene vapors. The product was then subjected to the usual treatment (Experiment 1) and to fractionation.

This gave 25 g (58.7%) of the β-diethylaminomethoxyethyl ether of dimethylethynylcarbinol (V) in the form of a slightly colored, mobile liquid.

B.p. 90-92° (5.5 mm), d_{20}^{20} 0.9030, n_D^{20} 1.4448, MR_D 62.80; calc. 62.84. Found%: N 6.57, 6.55. $C_{12}H_{23}O_2N$. Calculated%: N 6.57.

The β-diethylaminomethoxyethyl ether of dimethylethynylcarbinol reacted with a 2% aqueous solution of mercuric chloride with the formation of a white, clotted precipitate.

In addition to the main product, 3 g of the β-diethylaminomethoxyethyl ether of 1-diethylamino-4-methyl-2-pentyn-4-ol (VI) was obtained.

B.p. 129-130° (3 mm), n_D^{20} 1.4552. Found %: N 9.06, 9.09. $C_{17}H_{34}O_2N_2$. Calculated %: N 9.39.

b) In dioxane medium. Into a mixture of 25.6 g of the β-hydroxyethyl ether of dimethylethynylcarbinol, 7.2 g of paraformaldehyde, and 30 ml of dioxane, cooled with ice water, was introduced 16.06 g of diethylamine.

The process was carried out at the boiling point of the mixture (94°) for 8 hours. After appropriate treatment of the reaction product (Experiment 1), 3-fold distillation gave 16.5 g (55.4%) of β-diethylamino-4-methyl-2-pentyn-4-ol (VI), obtained in the form of a slightly colored, mobile liquid.

B.p. 129-130° (3 mm), d_{20}^{20} 0.9060, n_D^{20} 1.4553, MR_D 89.70; calc. 89.87. Found %: N 9.76, 9.46. $C_{17}H_{34}O_2N_2$. Calculated %: N 9.39.

6. Aminomethylation of β-cyanoethyl ether of dimethylethynylcarbinol in benzene medium (Cf. [1]). 20.55 g of the β-cyanoethyl ether of dimethylethynylcarbinol, 12.05 g of diethylamine, 5.4 g of paraformaldehyde, and 75 ml of benzene were heated at the boiling point in a flask fitted with a water trap. The water formed during the reaction was removed by benzene vapors. Treatment and isolation of the reaction product was carried out as usual (Experiment 1).

Vacuum fractionation gave the following fractions: 1st, 80-82° (25 mm), n_D^{20} 1.4289, 3.4 g; 2nd, 93-101° (25 mm), n_D^{20} 1.4374, 11 g; 3rd, 101-134° (25-26 mm), n_D^{20} 1.4489, 3.7 g; 4th, 134° (6 mm), n_D^{20} 1.4598, 9.5g; residue 4 g.

The 1st fraction was tetraethyldiaminomethane [5, 7]. The 2nd fraction, according to boiling point and index of refraction, was the unreacted, original β-cyanoethyl ether of dimethylethynylcarbinol [1]; this was confirmed by analysis.

Found %: N 10.54, 10.73 $C_9H_{11}ON$. Calculated %: N 10.22.

The 4th fraction, b. p. 134° (6 mm), was the β-cyanoethyl ether of 1-diethylamino-4-methyl-2-pentyn-4-ol [1]. The yield was 28.3%.

Found %: N 12.60, 12.67. $C_{13}H_{22}ON_2$. Calculated %: N 12.61.

SUMMARY

1. It was shown that tertiary acetylenic alcohols smoothly undergo aminomethylation at the hydroxyl hydrogen with the formation of diethylaminomethyl ethers.

2. The aminomethyl derivatives of tertiary acetylenic alcohols obtained during the work have not been described in the literature.

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Scientific Research Institute of
Plastic Materials

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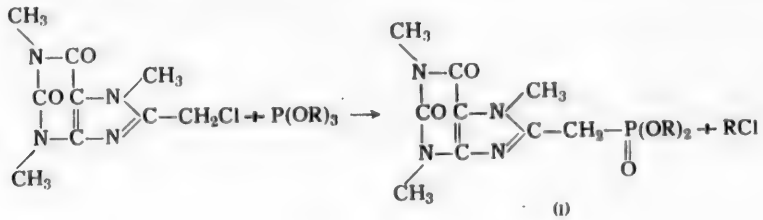
SYNTHESIS OF ESTERS OF 8-METHYLCAFFEINEPHOSPHONIC ACID

B. P. Lugovkin

Caffeine and certain of its derivatives such as, for example, 8-methylcaffeine find valuable application in medicine [1]; as a result of this, the study of caffeine derivatives is of specific interest. In one of her published works, E. S. Golovchinskaya [2] described the synthesis and chemical properties of 8-chloromethylcaffeine. The chlorine atom in this compound showed great reactivity in a number of reactions carried out by this author [3].

It was of interest to us to study the reaction of 8-chloromethylcaffeine with esters of phosphorus acid. There are no data available in the literature regarding organophosphorus derivatives of caffeine.

We were able to prepare the diethyl, dipropyl, diisopropyl, dibutyl, and diisobutyl esters of 8-chloromethylcaffeine (I) by means of the A. E. Arbuzov reaction [4].



(I)

Derivative	Melting point	Yield (in %)	P content (%)	
			Found	Calcd.
$R = OC_2H_5$	133°	96.7	9.31	9.0
$R = OC_3H_7$	70—71	65.2	8.18	8.32
$R = OC_3H_7$-iso	121—122	85.6	8.10	8.32
$R = OC_4H_9$	Viscous liquid	88.8	7.80	7.73
$R = OC_4H_9$-iso	75—76	88.7	7.91	7.73
R = OH *	285—286	93.3	9.91	10.75

* This material did not contain chloride iron (Carius method).

The reaction proceeds with quantitative yields of the esters on heating the components in the range of 150-195°.

Attempts to synthesize tetraethyldiphosphono-8-methylcaffeine and the diethyl ester of 8-chloromethylcaffeinephosphonic acid by heating 8-dichloromethylcaffeine [3] with triethyl phosphite (2 moles) at 152° were unsuccessful.

Except for the dibutyl ester, these esters are crystalline materials, and are soluble in water, alcohol, acetone, ether, and benzene. 8-Methylcaffeinephosphonic acid is obtained by hydrolysis of the esters with hydrochloric acid.

The experimental results are presented in the table.

EXPERIMENTAL

The starting material, 8-chloromethylcaffeine, was prepared by chlorination of 8-methylcaffeine* using the method developed by E. S. Golovchinskaya and E. S. Chaman [2]. After the appropriate reactions, the chloride was recrystallized from glacial acetic acid (m. p. 215°).

The experiments were carried out in a Claisen flask with the outlet tube sealed low (for distillation of the alkyl chloride). A thermometer was inserted into the flask. Heating was carried out on a molten-metal bath (Wood's alloy) until evolution of alkyl chloride was complete.

Synthesis of the diethyl ester of 8-methylcaffeinephosphonic acid. A mixture of 1.5 g of the chloride and 1.4 g of triethyl phosphite was heated at 152-155° for 10 minutes (vigorous evolution of ethyl chloride). The temperature was then increased to 180°. The reaction product, in the form of a viscous liquid, was dissolved in anhydrous alcohol and heated with activated carbon. After elimination of the solvent, the crystalline product was washed with a small amount of absolute ether. 2.05 g of material was obtained.

Synthesis of the dipropyl and diisopropyl esters was carried out under nearly the same conditions. A mixture of 1.5 g of the chloride and 1.6 g of the trialkyl phosphite was heated at 175-180° for 15 minutes (just as in the first experiment, vigorous evolution of alkyl chloride was observed). Subsequent treatment was analogous to that described above. The yield of dipropyl ester was 1.5 g; that of diisopropyl ester was 1.97 g.

After elimination of the solvent (alcohol) the dipropyl ester crystallized on long standing (crystallization was somewhat accelerated by grinding with anhydrous ether).

Synthesis of the dibutyl ester. A mixture of 2 g of the chloride and 2.06 g of tributyl phosphite was heated at 175-180° for 15 minutes (vigorous evolution of butyl chloride). The reaction product was dissolved in anhydrous ether (10 ml) and heated with activated carbon. 2.93 g of the dibutyl ester was obtained in the form of a very viscous, light yellow liquid.

Synthesis of the diisobutyl ester. A mixture of 1.5 g of the chloride and 1.9 g of triisobutyl phosphite was heated at 190-195° for 10 minutes (vigorous evolution of isobutyl chloride). The reaction product, in the form of a very viscous liquid, was dissolved in 5 ml of anhydrous ether. After elimination of the solvent and standing for a short while, 2.2 g of light yellow crystals was obtained. Colorless crystals were separated after heating in anhydrous alcohol with activated carbon.

Hydrolysis of the esters. 1.87 g of the dibutyl ester and 10 ml of dilute hydrochloric acid (1 : 1) were heated in a sealed tube at 110-120° for 5 hours. A crystalline product was obtained by repeated concentration by heating with water on a water bath. After recrystallization from acetic acid, 1.26 g of light yellow crystals was obtained. Colorless crystals were obtained by a second recrystallization. On heating, 8-methylcaffeinephosphonic acid dissolves in water and acetic acid and, with difficulty, in alcohol and glacial acetic acid; it is insoluble in anhydrous ether.

Hydrolysis of the remaining esters was carried out in a similar manner.

* It is our agreeable duty to express our deep appreciation to O. Yu. Magidson and E. S. Golovchinskaya for the gift of 8-methylcaffeine.

SUMMARY

1. The diethyl, dipropyl, diisopropyl, dibutyl, and diisobutyl esters of 8-methylcaffeinephosphonic acid were synthesized by the interaction of trialkyl phosphites with 8-chloromethylcaffeine.

2. 8-Methylcaffeinephosphonic acid was obtained by hydrolysis of these esters.

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[1] A. P. Orekhov, The Chemistry of Alkaloids,* ONTI 512 (1938); E. S. Golovchinskaya, J. Gen. Chem. 18, 2129 (1948); E. S. Golovchinskaya and O. Yu. Magidson, Author's Certificate 64, 625 (1945).

[2] E. S. Golovchinskaya and E. S. Chaman, J. Gen. Chem. 22, 537 (1952).**

[3] E. S. Golovchinskaya, J. Gen. Chem. 18, 2129 (1948).

[4] A. E. Arbuzov, Dissertation: "The Structure of Phosphorus Acid and Its Derivatives," St. Petersburg (1905).

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* In Russian.

** Original Russian pagination. See C. B. Translation.

THE REACTION OF ACETYLENIC AND VINYLACETYLENIC EPOXIDES WITH AMMONIA AND AMINES.

THE SYNTHESIS OF ALKYL-, VINYL, AND PHENYLPYRROLES AND PYRRYLCARBINOLS

F. Ya. Perveev, E. M. Vekshina and L. N. Surenkova

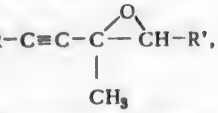
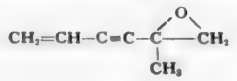
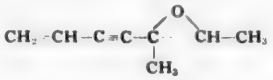
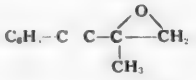
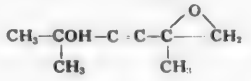
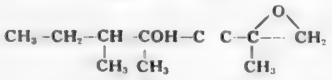
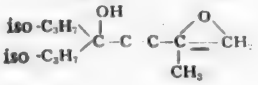
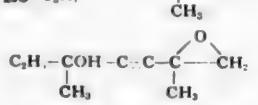
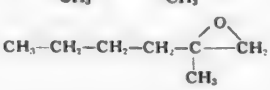
Previous work has shown that the reaction of hydrogen sulfide and of hydrogen selenide with epoxides and hydroxy epoxides [epoxyalcohols] of the acetylenic and vinylacetylenic series of the type  , where R is vinyl, alkyl, phenyl, etc., leads to the formation of the corresponding thiophene and selenophene homologs. With the aim of the further study of this reaction, we considered it expedient to investigate the conditions for cyclization of α-amino alcohols and α-alkyl-α-hydroxy amines. The epoxides presented in Table 1 were used as starting products.

TABLE 1

Epoxide No.	Formula	Name
(I)		2-Methyl-1,2-epoxy-5-hexen-3-yne
(II)		3-Methyl-2,3-epoxy-6-hepten-4-yne
(III)		2-Methyl-4-phenyl-1,2-epoxy-3-butyne
(IV)		2,5-Dimethyl-1,2-epoxy-3-hexyn-5-ol
(V)		2,5,6-Trimethyl-1,2-epoxy-3-octyn-5-ol
(VI)		2,6-Dimethyl-5-isopropyl-1,2-epoxy-3-heptyne-5-ol
(VII)		2,5-Dimethyl-1,2-epoxy-3-heptyn-5-ol
(VIII)		2-Methyl-1,2-epoxyhexane

During the study of the reaction of the enumerated epoxides with ammonia, ethylamine, and diethylamine, it was established that the rate of addition of the ammonia and amines depends on the structure of the particular epoxide. Thus, with epoxide (I) the reaction is completed in 8 hours at room temperature. Under these same conditions, epoxide (II) is only 50% reacted after 8 days. The epoxy alcohols (IV-VIII) react with ammonia and amines at a considerably greater rate than does epoxide (I). Epoxide (III) and the saturated epoxide (VIII) add practically no ammonia or amine at room temperature. The reaction proceeds to completion on lengthy heating above 100° in a sealed tube. The addition of diethylamine to epoxide (I) proceeds more slowly than does the addition of ammonia (1/3 of the epoxide is reacted after 46 hours). The addition of alkaline catalysts has practically no effect on the addition of ammonia or amines.

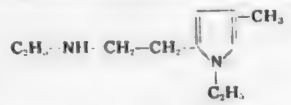
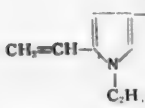
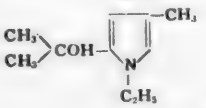
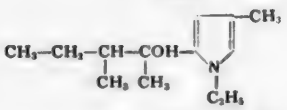
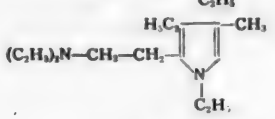
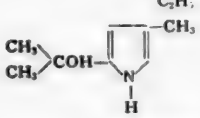
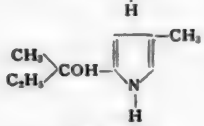
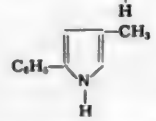
The reaction of epoxides and epoxyalcohols with ammonia and with amines leads to the formation of α-amino alcohols and aminoglycols. The constants of the amino alcohols synthesized are presented in Table 2. The unsaturated amino alcohols obtained (IX and X) are liquids with an unpleasant odor; they are soluble in water, ether, and alcohol. They polymerize on long-term storage, forming a glassy, brittle mass. Epoxide (IX) crystallized after a day; m. p. 44.5-45.5°. It hydrogenated completely over Raney Ni in a bomb at 122 atm. pressure and a temperature of 50-55°. Hydrogenation at ordinary temperature and pressure over Raney Ni proceeded very sluggishly. The reaction of (IX) with α-naphthyl isocyanate gave a crystalline product with m.p. 115-116° (urea derivative). A mixture of the urea derivatives obtained from the hydrogenation products of unsaturated amino alcohol (IX) and the saturated amino alcohol (XI) showed no depression of the melting point. The agreement of the physical constants of the hydrogenation product and 1-amino-2-methyl-2-hexanol and the absence of a melting point depression with the mixed sample indicate that these substances are identical.

TABLE 2

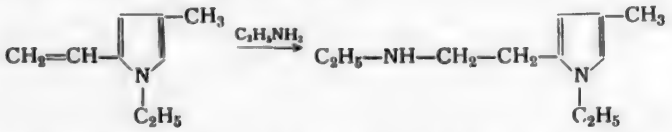
Compound No.	Formula	Boiling point (mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.
(IX)	$CH_2=CH-C\equiv C-\underset{\displaystyle CH_3}{\underset{\vert}{C}}OH-CH_2NH_2$	91—92° (4)	1.5165	1.0078	36.4	37.5
(X)	$CH_2=CH-C\equiv C-\underset{\displaystyle CH_3}{\underset{\vert}{C}}OH-CHNH_2-CH_3$	97—98 (7)	1.5061	0.9771	41.62	42.47
(XI)	$CH_3-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{C}}OH-CH_2NH_2$	85—86 (7)	1.4540	0.9045	39.47	39.29
(XII)	$CH_2=CH-C\equiv C-\underset{\displaystyle CH_3}{\underset{\vert}{C}}OH-CH_2-NH-C_2H_5$	60—61 (0.5)	1.4894	0.9271	46.4	47.8
(XIII)	$CH_3-CH-C\ C-\underset{\displaystyle CH_3}{\underset{\vert}{C}}OH-CH(NHC_2H_5)-CH_3$	64—66 (0.5)	1.4858	0.9169	51.15	52.04
(XIV)	$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{COH}}-C\equiv C-\underset{\displaystyle CH_3}{\underset{\vert}{COH}}-CH_2-NHC_2H_5$	14—115 (0.5)	1.4752	0.9537	67.11	67.08
(XV)	$C_6H_5-C-C-\underset{\displaystyle CH_3}{\underset{\vert}{C}}OH-CH_2-NH_2$	M.p. 120—121	—	—	—	—
(XVI)	$CH_2=CH-C=\underset{\displaystyle CH_3}{\underset{\vert}{C}}OH-CH_2N\begin{matrix}C_2H_5\\C_2H_5\end{matrix}$	92—93 (7)	1.4762	0.8915	55.99	57.36

Amino alcohols (IX and X) have low thermal stability. They decompose completely on heating in a vacuum above 140°. They do not form picrates. Ethylamines (XII and XIII) are more mobile liquids than (IX and X); they are more difficultly oxidized in air, and they show less tendency toward polymerization. They are thermally very stable. Ethylamino glycol (XIV) is a sirup-like, viscous liquid with a greenish yellow color.

Lengthy heating of the epoxides in sealed tubes on a water bath with quinoline plus an excess of amine or amino alcohol results in the formation of the corresponding homologs of pyrrole (Table 3). Pyrroles were also obtained by treatment of the amino alcohols with steam in the presence of barium hydroxide with a constant volume of the reaction mixture. We were unable to isolate N-ethylvinylpyrrole after heating epoxides (I and II)

Compound No.	Formula	Boiling point (mm)	n_D^{20}	d_4^{20}	MR_D Calc.	MR_D Found
(XVII)		103—104° (0.5)	1.4950	0.9162	57.30	57.15
(XVIII)		58 (1)	1.5326	0.9170	44.2	45.6
(XIX)		m.p. 46—48	—	—	—	—
(XX)		106—108 (0.5)	1.4902	0.9395	64.5	64.7
(XXI)		95—99 (0.5)	1.4974	0.9191	75.52	75.40
(XXII)		m.p. 50.5—51	—	—	—	—
(XXIIII)		Easily fusible crystals which form tar during distillation				
(XXIV)		M. p. 152	—	—	—	—

with ethylamine at elevated temperature (100°). Under these conditions, the reaction of the epoxides with ethylamine leads to the formation of ethylaminopyrrole. Thus, typical nucleophilic reagents (ammonia and amines) which do not add to an isolated multiple bond of olefins under the same conditions, readily add to a vinyl group in the α-position in the pyrrole ring, just as they do to ethylene derivatives having an electrophilic substituent (acrylic acid, acrolein, nitroethylene, vinyl cyanide).

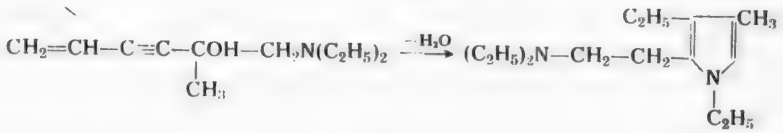


The course of the addition of ethylamine to the side chain is still unresolved. The question arises as to whether the ethylamine is added to the aminoalcohol simultaneously with cyclization or after the formation of the five-membered ring. With the aim of clarifying this problem, N-ethyl-2-vinyl-4-methylpyrrole (XVIII), synthesized by us, was heated with ethylamine in a sealed tube on a boiling water bath. The properties of the isolated reaction product corresponded completely to those of N-ethyl-2-ethylaminoethyl-1, 4-methylpyrrole; consequently, the addition of ethylamine to the double bond occurs after ring closure.

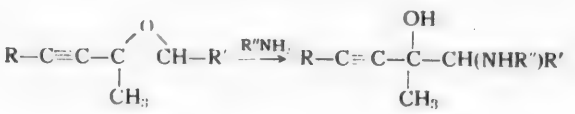
2-Vinyl-4-methylpyrrole is an unstable compound which polymerizes on distillation; therefore, it cannot be isolated in the pure state. Pyrrylcarbinol (XXII) is also an extremely unstable compound, darkening rapidly in air, and converting, after a day, to a frangible, brown powder which does not sublime under vacuum. Pyrrylcarbinol (XXIII) is still less stable. During vacuum distillation, it is converted to a tarry mass. The introduction

of an ethyl group into the N-position considerably increases the stability of vinylpyrroles and pyrrylcarbinols. Thus, for example, compounds (XVIII) and (XIX) are stable, and do not undergo appreciable change during long-term storage.

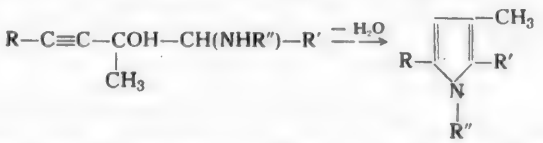
N-ethylpyrrylcarbinol is formed by the action of an excess of ethylamine on the epoxide in sealed tubes at an elevated temperature. Of particular interest is the synthesis of N-ethyl-2-(β-diethylaminoethyl)-4-methylpyrrole by the action of diethylamine on oxide (I), since here the formation of the heterocyclic compound is associated with migration of the ethyl group from the nitrogen atom.



On the basis of the data obtained, it can be considered as established that the addition of ammonia and diethylamine to disubstituted unsymmetrical epoxides and epoxy alcohols of the acetylene and vinylacetylene series proceeds according to the rule of Krasussky;** i. e., opening of the epoxide ring occurs at the more hydrogenated carbon atom,



since the formation of pyrroles is possible only from amino alcohols of the above structure



where: R is vinyl, alkyl, hydroxyalkyl, or hydrogen; R' is alkyl or hydrogen; R" is alkyl or hydrogen.

Comparing the data obtained with data relating to the conversion of epoxides of the acetylene and vinylacetylene series to heterocyclic compounds under the influence of hydrogen selenide and of hydrogen sulfide [1] and also with data relating to the cyclization of α-acetylenic glycols [2], it can be concluded that the tendency of these compounds toward cyclization depends on the nature of the hetero atom occurring in the system $R-C\equiv C-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}OH-CH(XH)-R'$, where X = O, N, S, Se.

The hetero atoms can be arranged in the following order of decreasing effect on cyclization: Se > S > N > O. Thus, hydroxyselenols and hydroxymercaptans cannot be isolated in the free state; under reaction conditions (30-40°), they are converted to five-membered heterocycles. Hydroxy- and alkylhydroxyamines are stable compounds; they cyclize at 100° under the influence of organic bases. α-Glycols, even on lengthy heating at a temperature of 180-200° in the presence of quinoline, do not undergo any changes with the exception of a small amount of tar formation.

The observed regularities can be formulated as follows. The cyclizing effect of the hetero atoms present in the system is greater the less its electronegativity: O (80.7), N (69.2), S (57.7), Se (55.4)*, since a decrease in the electronegativity of the hetero atom increases the electron density at the carbon atom connected to the hydroxyl group.

* The electronegativity of these elements is given in electron volts.
** Transliteration of Russian — Publisher's note.

EXPERIMENTAL

Preparation of 1-amino-2-methyl-2-hydroxy-5-hexen-3-yne (IX). 200 ml of 30% aqueous ammonia and 25 g of epoxide (I) were placed in a round-bottomed flask fitted with a mechanical stirrer. The reaction mixture was stirred for a period of several hours at room temperature. The reaction was considered complete when the epoxide had completely dissolved. The water and excess ammonia were distilled under vacuum, and the dark brown liquid remaining in the flask was dissolved in ether. The ethereal solution was dried over $MgSO_4$, the ether eliminated, and the product distilled under vacuum. 20 g of the hydroxyamine was isolated (69%).

Found %: C 67.35; H 8.75, N 10.80, 10.70; act. H 1.739, 1.750. $C_7H_{11}ON$. Calculated %: C 67.2; H 8.8; N 11.19; act H 1.613.

Hydrogenation. 9.5 g of hydroxyamine (IX) was dissolved in methyl alcohol and hydrogenated over Raney Ni in a rotating bomb at 50-55° and an initial pressure of 120 atm. After 4 hours, the hydrogenation pressure had decreased to 91 atm., and it then remained constant for an hour. 10,850 ml of hydrogen was absorbed. 10,500 ml of hydrogen is required for hydrogenation of the double and triple bonds. After distillation of the alcohol, the resulting product, 1-amino-2-methyl-2-hydroxyhexane (XI) was dried and distilled under vacuum.

Found%: N 10.88, 10.83. $C_7H_{17}ON$. Calculated %: N 10.78.

The substance formed a crystalline urea derivative with α-naphthyl isocyanate in petroleum ether. After recrystallization from benzene, the resulting white crystals had a m. p. of 115-116°.

Found %: N 9.55, 9.40. $C_{18}H_{24}O_2N_2$. Calculated %: N 9.33.

Preparation of 2-amino-3-methyl-3-hydroxy-6-hepten-4-yne (X). 100 ml of 30% aqueous ammonia and 10 g of epoxide (II) were used. The reaction mixture was stirred for 8 days. 5 g (43%) of hydroxyamine (X) was isolated.

Found %: N 10.21, 10.33; act. H 1.463. $C_8H_{17}ON$. Calculated %: N 10.06; act. H 1.448.

Preparation of 1-amino-2-methyl-2-hydroxyhexane (XI). 20 g of the saturated epoxide (III) and 60 ml of 30% aqueous ammonia were heated in a sealed tube at 100° for a period of 25 hours. After distillation of the residual ammonia and water, 8 g of the amino alcohol was isolated.

Found %: N 10.78; act. H 1.5085. $C_7H_{17}ON$. Calculated %: N 10.68; act. H 1.536

By the reaction of α-naphthyl isocyanate in petroleum ether with the hydroxyamine, a urea derivative was obtained—a crystalline substance with a m. p. of 114-115° (recrystallized from benzene).

Preparation of 1-ethylamino-2-methyl-2-hydroxy-5-hexen-3-yne (XII). 10 g of epoxide (II), 5 g of ethylamine, and 1 ml of water were used. The reaction mixture was allowed to stand in a sealed tube at room temperature for 50-60 hours. The resulting material was distilled under vacuum. 9 g of product was isolated; it was a viscous liquid, difficultly soluble in water and readily soluble in organic solvents.

Found %: N 9.34, 9.01; number of act. H 0.717. $C_9H_{15}ON$. Calculated %: N 9.14; number of act. H 0.658.

Preparation of 2-ethylamino-3-methyl-3-hydroxy-6-hepten-4-yne (XIII). 5 g of ethylamine, 7 g of epoxide (II), and 1 ml of water were allowed to stand for 2 days in a sealed tube at room temperature. After 2-fold distillation under vacuum, 7.5 g of material was isolated. The product was a mobile, yellowish liquid, difficultly soluble in water and readily soluble in organic solvents.

Found %: C 71.80 H 10.28; N 8.25, 8.30; number of act. H 1.001, 1.003. $C_{10}H_{17}ON$. Calculated %: C 71.85; H 10.18; N 8.37; number of act. H 1.

Preparation of 1-ethylamino-2, 5, 6-trimethyl-2, 5-dihydroxy-3-octyne (XIV). 7 g of epoxide (V), 5 g of ethylamine, and 0.5 ml of water were used. The reaction mixture was allowed to stand for a day in a sealed tube at room temperature. Distillation gave 8 g of material. The product was a sirupy liquid with a greenish yellow color.

Found %: N 6.25, 6.28. $C_{13}H_{25}O_2N$. Calculated %: N 6.16

Preparation of 1-amino-2-methyl-2-hydroxy-4-phenyl-3-butyne (XV). 40 ml of 30% aqueous ammonia and 7 g of epoxide (III) were heated in a sealed tube at a temperature of 130-140° for a period of 10 hours. At the completion of the reaction and after cooling in the tube, white crystals precipitated, which were filtered and recrystallized from aqueous alcohol. The yield was 6 g.

Found %: N 8.05, 8.07. $C_{11}H_{13}ON$. Calculated %: N 8.0

Preparation of 1-diethylamino-2-methyl-2-hydroxy-5-hexene-3-yne (XVI). To a solution of 30 ml of diethylamine was added 15 g of epoxide (I), and the mixture was allowed to stand for 46 hours at room temperature. 6 g of unreacted epoxide and 10 g of alcohol (XVI) were recovered. After contacting the epoxide with the diethylamine for 4 days, the yield of tertiary amino alcohol (XVI) increased to 85%. If the reaction is carried out at 35-40°, the reaction time can be decreased to 8-10 hours.

Found %: C 66; H 9.59; N 7.76, 7.78; act. H 0.570. $C_{11}H_{19}ON$. Calculated %: C 66; H 9.5; N 7.73; act. H 0.556.

Preparation of N-ethyl-2-(β-ethylaminoethyl)-4-methylpyrrole (XVII). 10 g of epoxide (I), 10 g of ethylamine, and 1 ml of water were used. The reaction mixture was heated in a sealed tube for 8 hours on a boiling water bath. The resulting material was distilled under vacuum. 2-Fold distillation of the material gave 11 g of a mobile, yellowish liquid. The mercury derivative melted with decomposition at 75-77°. The material was colored dark violet by the action of an aqueous solution of SeO_2.

Found %: C 73.38; H 11.21; N 15.68, 15.88. $C_{11}H_{20}N_2$. Calculated %: C 73.33; H 11.11; N 15.66.

Preparation of N-ethyl-2-vinyl-4-methylpyrrole (XVIII). 6 g of ethylamino alcohol (XII) and 1 g of quinoline were used. The reaction mixture was heated in a sealed tube on a boiling water bath for 24 hours. The product was distilled under vacuum. There was obtained 4 g of a colorless, mobile liquid, insoluble in water and readily soluble in organic solvents. The mercury derivative melted with decomposition at 58-60°.

Found %: C 80.1; H 9.66; N 10.02, 10.15. $C_9H_{13}N$. Calculated %: C 80; H 9.63; N 10.36.

Preparation of N-ethyl-2-(hydroxyisopropyl)-4-methylpyrrole (XIX). 10 g of epoxide (IV), 6 g of ethylamine, and 1 ml of water were used. The reaction mixture, sealed in a tube, was allowed to stand at room temperature, 15-17°, for 8 hours. The resulting viscous, sirupy mass was heated on a boiling water bath for 10-12 hours. The resulting material was distilled under vacuum. The distillation product crystallized in the receiver. The substance was insoluble in water and readily soluble in ether, benzene, and other organic solvents; it sublimed under vacuum. The mercury derivative melted with decomposition at 50-52°. The yield was 8.5 g.

Found %: N 8.7, 8.4; number of act. H 1.01, 1.02. $C_{10}H_{17}ON$. Calculated %: N 8.37; number of act. H 1.

Preparation of N-ethyl-2-(1-hydroxy-1, 2-dimethyl)butyl-4-methylpyrrole (XX). The reaction mixture—9 g of epoxide (V), 6 g of ethylamine, and 1 ml of water—sealed in a tube, was heated on a boiling water bath for a period of 22 hours. The resulting product was distilled under vacuum. The material was a viscous, yellow liquid, insoluble in water, and readily soluble in ether and other organic solvents. The mercury derivative melted with decomposition at 126-128°. Boiling the material with an aqueous solution of SeO_2 gave the violet color characteristic of pyrroles.

Found %: N 6.59, 6.69; number of act. H 1.04, 0.99. $C_{13}H_{23}ON$. Calculated %: N 6.7; number of act H 1.

Preparation of 2-(1-hydroxyisopropyl)-4-methylpyrrole (XXII). 150 ml of 30% aqueous ammonia and 13 g of epoxide (IV) were placed in a 250-ml flask, and stirred for 8 hours. The temperature of the reaction mixture increased immediately to 27°, and then dropped to 10-15°. 25 g of $Ba(OH)_2$ was added to the solution. The reaction mixture was steam distilled at constant volume. White crystals separated out in the receiver. 7 g of material separated. On storage in air, the product rapidly darkened, and it did not sublime on standing for a day under vacuum; it was insoluble in water and readily soluble in ether or other organic solvents. This product is still less stable in solution than in the solid form. The solution darkens a minute after preparation, and practically no pyrrylcarbinol can be separated from the solvent. The mercury derivative melts with decomposition at 90-92°.

Found%: N 10.12, 10.21; act. H 0.774. $C_8H_{11}ON$. Calculated %: N 10.06; act. H 0.724.

Preparation of 2-(1-hydroxy-1-methyl)propyl-4-methylpyrrole (XXIII). The pyrrylcarbinol was synthesized by the above-described method. The resulting low-melting crystals were insoluble in water and readily soluble in organic solvents. Boiling with an aqueous solution of SeO_2 gave the violet color characteristic of pyrroles. Owing to the extreme instability of the material, we were unable to isolate it in the pure state.

Preparation of 2-phenyl-4-methylpyrrole (XXIV). 3 g of amino-alcohol (XV) was treated with steam in the presence of $Ba(OH)_2$. 2 g of crystalline product was isolated; this product gave the violet color characteristic of pyrroles when boiled with an aqueous solution of SeO_2. A mixture of this material with 2-phenyl-4-methylpyrrole prepared by another method [3] showed no depression of the melting point.

Found %: N 8.88, 8.90. $C_{11}H_{11}N$. Calculated%: N 9.91.

Preparation of N-ethyl-2-(β-diethylaminoethyl)4-methylpyrrole (XXI). 10 g of epoxide (I), 8 g of diethylamine, and 0.5 ml of water were heated in a sealed tube on a boiling water bath for a period of 20 hours. 6 g of product was obtained. On boiling with an aqueous solution of SeO_2, the aminopyrrole gave the violet color characteristic of pyrroles. The mercury derivative melted with decomposition.

Found%: C 75.14; H 11.55; N 13.35, 13.39. $C_{13}H_{24}N_2$. Calculated%: C 75; H 11.53; N 13.46.

SUMMARY

1. The synthesis of amino- and alkylamino alcohols of the acetylenic and vinylacetylene series was carried out for the first time: 1-amino-2-methyl-2-hydroxy-5-hexen-3-yne, 2-amino-3-methyl-3-hydroxy-6-hepten-4-yne, 1-amino-2-methyl-2-hydroxyhexane, 1-ethylamino-2-methyl-2-hydroxy-5-hexen-3-yne, 2-ethylamino-3-methyl-3-hydroxy-6-hepten-4-yne, 1-ethylamino-2, 5, 6-trimethyl-2, 5-dihydroxy-3-octyne, 1-amino-2-methyl-2-hydroxy-5-phenyl-3-butyne, and 1-diethylamino-2-methyl-2-hydroxy-5-hexen-3-yne.

2. It was established that the addition of ammonia and amines to disubstituted, unsymmetrical epoxides and epoxy alcohols of the acetylene and vinylacetylene series proceeds according to Krasusky's rule.

3. A new method was developed for the preparation of alkylpyrroles, and of N-alkyl substituted vinylpyrroles, and pyrrylcarbinols. Using this method, the synthesis of a number of pyrrole derivatives was carried out; seven of these have not been described in the literature, namely: N-ethyl-2-(β-ethylaminoethyl)-4-methylpyrrole, N-ethyl-2-vinyl-4-methylpyrrole, N-ethyl-2-hydroxyisopropyl-4-methylpyrrole, N-ethyl-2-(1-hydroxy-1, 2-dimethyl)butyl-4-methylpyrrole, N-ethyl-2-(β-diethylaminoethyl)-4-methylpyrrole, 2-(1-hydroxyisopropyl)-4-methylpyrrole, and 2-(1-hydroxy-1-methylpropyl)-4-methylpyrrole.

4. It was found, for the first time, that vinyl pyrroles readily add amines at the double bond.

5. It was found that the transformation of dialkylamino alcohols of the acetylene and vinylacetylene series proceeds as a consequence of the migration of the alkyl radical from the nitrogen atom.

6. It was established that the cyclizing effect of a hetero atom occurring in the system $R-C\equiv C-\underset{\underset{CH_3}{|}}{COH}-CH(XH)-R'$, is greater the less its electronegativity.

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SYNTHESIS OF α-(TRIMETHYLSILYL) STYRENE, 1-(TRIMETHYLSILYL) CYCLOHEXENE, AND OTHER UNSATURATED ORGANOSILICON COMPOUNDS

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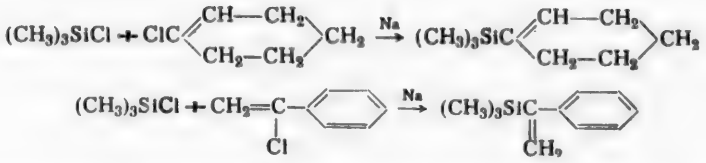
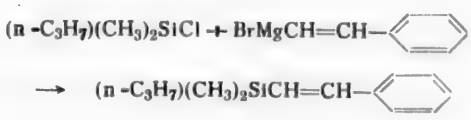
Continuing our investigation on organosodium synthesis of unsaturated organosilicon compounds [1], in the present work we attempted to use a number of new unsaturated halogen-containing compounds in this synthesis. It was shown that both 1-chlorocyclohexene and α-chlorostyrene readily undergo condensation with trimethylchlorosilane.



The first representatives of unsaturated silicohydrocarbons containing cyclohexenyl and α-styryl radicals were obtained in this manner. However, though the yield of the first-mentioned silicohydrocarbon was 70%, that of the second was only 30%, since the preparation of the monomer was accompanied by the formation of polymer.

A still greater yield of polymer was formed when β-bromo or chlorostyrene was used instead of α-chlorostyrene. For this reason, we were able to prepare pure α-(propyldimethylsilyl) styrene only by organomagnesium synthesis



Until the present work, only two silicohydrocarbons containing a styrene radical were known: $(C_6H_5)_3SiCH=CHC_6H_5$ [2] and $(CH_3)_3SiCH=CHC_6H_5$ [3]. Our attempt to carry out with the aid of sodium the condensation of R_3SiCl with $R_3SiOCH_2C\equiv CCH_2Cl$ was unsuccessful owing to high tar formation. Attempts to use the compounds $(RO)_3SiCH=CHCl$ and $(RO)_3SiCCl=CH_2$ in the organosodium synthesis also ended in failure.

In the present work, we prepared a series of compounds of the type $R_3SiCH=CH_2$, where R is CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9, and we obtained more precise values of their physical constants, which, for the latter two compounds, diverged sharply from the values given in the literature (see table). We were unable to prepare compounds with two vinyl radicals, $R_2Si(CH=CH_2)_2$, by either organosodium or organomagnesium [4] synthesis owing to their vigorous polymerization during the reaction. In these experiments, it was observed that, with ethyl acetate initiation, $(C_2H_5)_2SiCl_2$ vigorously reacts in toluene with metallic sodium forming condensation products with a wide boiling range and molecular weights up to 1200. It is well known that $(CH_3)_2SiCl_2$ also reacts with sodium, but severe experimental conditions are required for this [5]. In a preceding paper, we reported that dialkyldithiophosphoric acids, $(RO)_2PS_2H$, readily add to various alkenylsilanes [6]. Compound XVII (see table) was

prepared in a similar manner by mixing equimolar amounts of methylphenyldiallylsilane and dimethyl hydrogen dithiophosphate. It was shown that thioacetic acid also adds to $(CH_3)_3SiCH_2CH{=}CH_2$, with simple mixing, the reaction being accompanied by the evolution of heat.

$$(CH_3)_3SiCH_2CH{=}CH_2 + HSC(=O)CH_3 \longrightarrow (CH_3)_3SiCH_2CH(CH_3)SC(=O)CH_3$$

The properties of 6 previously prepared compounds, more accurately characterized in the present work, and also of 12 compounds which were synthesized for the first time are presented in the table.

EXPERIMENTAL

Butyldimethylchlorosilane (V). $n\text{-}C_4H_9MgBr$, prepared from 73 g of Mg and 500 g of $n\text{-}C_4H_9Br$ in 1 liter of ether, was added to 450 g of dimethyldichlorosilane. 215 g of butyldimethylchlorosilane was obtained. Propyldimethylchlorosilane (VI) and propyldiethylchlorosilane (VII) (see table) were prepared under similar conditions.

Tributylvinylsilane (IV). 65 g of vinyltrichlorosilane was added to $n\text{-}C_4H_9MgBr$ prepared from 36 g of Mg and 262 g of $n\text{-}C_4H_9Br$ in 0.5 liter of ether. After 5 hours refluxing, the contents of the flask were decomposed with water. The ether layer, together with the ethereal extracts of the water layer, was dried with $CaCl_2$. Distillation under vacuum gave 71 g of tributylvinylsilane. Trimethylvinylsilane (I), triethylvinylsilane (II), and tripropylvinylsilane (III) were prepared in a similar manner.

Trimethyl(1-cyclohexenyl)silane (X). 23 g of sodium was melted in 100 ml of o-xylene and dispersed by a rapidly rotating stirrer. After cooling, the o-xylene was replaced by 200 ml of ether, and 50 g of trimethylchlorosilane, 5 ml of 1-chlorocyclohexene [7], and 2 ml of ethyl acetate were added to the flask. When the reaction had begun, the addition of 60 g of 1-chlorocyclohexene was continued for 2 hours while stirring. On the following day, the liquid was filtered from the residue, which was washed with fresh ether. Distillation in a column gave 50 g of (X).

Found%: C 69.63, 69.76; H 11.91, 11.87 Si 17.87; 17.90. $C_9H_{18}Si$. Calculated %: C 70.05; H 11.75; Si 18.18.

Raman spectrum: 215(4b), 266(1), 298(2), 321(0), 355(2), 381(0), 402(0), 439(1), 491(1b), 539(3), 632(5), 660(0), 694(3), 729(0), 753(1), 837(3b), 855(2), 911(2), 943(1), 970(1), 1000(1),1039(2), 1079(2b), 1124(0), 1179(2), 1195(1), 1251(1), 1271(3), 1308(2), 1554(2b), 1377(1), 1409(0), 1425(4), 1448(1), 1460(1), 1620(4), 1575(0), 1553(0), 2833(4), 2865(3), 2900(10), 2933(2), 2957(9), 3005(2), 3032(1).

Trimethyl-α-styrylsilane (VIII). 60 g of trimethylchlorosilane was added to 30 g of Na in 250 ml of ether, and then 69 g of α-chlorostyrene [8] was added over a period of 40 minutes. After two days and after the usual treatment in the presence of hydroquinone, 32 g of trimethyl-α-styrylsilane was obtained by vacuum distillation. 28 g of a transparent, light yellow polymer remained in the bottoms.

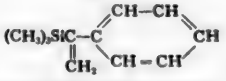
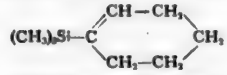
Found%: C 75.08, 74.89; H 9.09, 9.15; Si 15.58, 15.58. $C_{11}H_{16}Si$. Calculated %: C 74.92; H 9.14; Si 15.92.

Propyldimethyl-β-styrylsilane (IX). 30 g of propyldimethylchlorosilane was added to $C_6H_5CH{=}CHMgBr$ prepared from 6.3 g of Mg and 57 g of β-bromostyrene in 250 ml of ether. The ether was then distilled, and the residue in the flask was heated on a boiling water bath for 6 hours. After recovery of the ether by distillation, the contents of the flask were decomposed with water. Distillation under vacuum gave 12 g of (IX).

Found%: C 76.50, 76.55: H 9.41, 9.42; Si 13.23, 13.10. $C_{13}H_{20}Si$. Calculated %: C 76.40; H 9.86; Si 13.73.

1, 2-Bis(trimethoxysilyl)ethylene (XI). 33 g of bis(trichlorosilyl)ethylene [9] was slowly added to a mixture consisting of 250 g of absolute methyl alcohol, 70 g of pyridine, and 250 ml of benzene. After two days, the residue was filtered and washed with fresh benzene. After distillation of the benzene, rectification under vacuum gave 22.5 g of (XI).

Found %: C 35.79, 36.14; H 7.59, 7.61; Si 20.58, 20.68. $C_8H_{20}O_6Si_2$. Calculated %: C 35.80; H 7.51; Si 20.91.

No.	Formula of compound	Boiling point (mm)	n_D^{20}	d_4^{20}	MR_D Found	MR_D Calc.	Yield (%)
I*	$(CH_3)_3SiCH{=}CH_2$	54.6° (744)	1.3910	0.6903	34.49	34.44	65
II**	$(C_2H_5)_3SiCH{=}CH_2$	146.5 (750)	1.4345	0.7728	47.99	47.97	67
III***	$(n\text{-}C_3H_7)_3SiCH{=}CH_2$	198.2 (758.5)	1.4430	0.7852	62.25	62.22	51.5
IV****	$(n\text{-}C_4H_9)_3SiCH{=}CH_2$	128 (16), 123 (13)	1.4494	0.7988	76.11	76.11	78.9
V*****	$(n\text{-}C_4H_9)(CH_3)_2SiCl$	138.4 (747)	1.4205	0.8751	43.62	43.72	47.5
VI	$(n\text{-}C_3H_7)(CH_3)_2SiCl$	113.8 (736)	1.4138	0.8726	39.12	39.07	37.5
VII******	$(n\text{-}C_3H_7)(C_2H_5)_2SiCl$	166.4 (739)	1.4347	0.9024	47.60	47.90	21.2
VIII		52 (3)	1.5115	0.8866	59.62	58.68	36.5
IX	$(n\text{-}C_3H_7)(CH_3)_2SiCH{-}CHC_6H_5$	133 (18)	1.5218	0.8908	69.96	67.94	26.5
X		171.5 (752)	1.4628	0.8351	50.86	50.83	70.5
XI	$(CH_3O)_2SiCH{=}CHSi(OCH_3)_3$	80 (2), 228—229 (743)	1.4155	1.0721	62.74	62.52	75
XII	$(CH_3O)_2SiCCl{-}CH_2$	157.4 (743)	1.4183	1.1109	41.46	41.56	50
XIII	$(CH_3O)_2SiCH{-}CHCl$	164 (746)	1.4195	1.1097	41.61	41.56	41
XIV	$(C_2H_5O)_2SiCCl{-}CH_2$	184 (753)	1.4161	1.0145	55.60	55.45	—
XV	$(CH_3)_2SiOCH_2C{=}CCH_2Cl$	71 (6)	1.4538	0.9988	47.89	48.16	45
XVI	$(CH_3)_2(C_2H_5)SiOCH_2C{=}CCH_2Cl$	58 (2)	1.4593	0.9965	52.35	52.67	40
XVII	$(C_6H_5)(CH_3)Si[CH_2CHSP(OCH_3)_2]_2$ (CH$_3$, S)	— —	1.5550	1.1799	141.09	141.16	90
XVIII	$(CH_3)_3SiCH_2CHSCCH_3$ (CH$_2$, O)	126—127 (60)	1.4652	0.9198	57.23	56.65	87

* From [3]: B. p. 55° (739 mm), n_D^{20} 1.3902, d_4^{20} 0.6903, MR_D 34.43; α [11]: B.p. 54.4° (754 mm), n_D^{25} 1.3880, d_4^{25} 0.6865, MR_D 34.44; α [12]: B.p. 55.5° (767 mm), n_D^{20} 1.3914, d_4^{20} 0.6910, MR_D 34.50.

** From [11]: B.p. 144° (740), n_D^{25} 1.4340, d_4^{25} 0.7674, MR_D 48.29; α [12]: B.p. 143.2° (755 mm), n_D^{20} 1.4330, d_4^{20} 0.7847, MR_D 47.13; α [13]: B.p. 146° (760 mm) n_D^{20} 1.4330, d_4^{20} 0.6653, MR_D 47.70.

*** From [11]: B.p. 73.0° (4.5 mm), n_D^{25} 1.4432, d_4^{25} 0.8310, MR_D 58.85.

**** From [11]: B.p. 99.0° (6.5 mm), n_D^{25} 1.4479, d_4^{25} 0.8261, MR_D 73.17

***** From [14]: B.p. 138.2-138.3° (751.5), n_D^{20} 1.4208, d_4^{20} 0.8766, MR_D 43.59.

****** From [15]: B.p. 164-166° (742 mm).

α-Chlorovinyltrimethoxysilane (XII). 56 g of α-chlorovinyltrichlorosilane [9] was added to a mixture consisting of 66 g of pyridine, 35 g of absolute methyl alcohol, and 100 ml of benzene. On the following day, after the usual treatment, 26.5 g of the substance was obtained.

Found %: C 33.06, 32.82; H 6.05, 6.04; Cl 19.34, 18.93; Si 15.59, 15.77. $C_5H_{11}O_3SiCl$. Calculated %: C 32.87; H 6.07; Cl 19.41; Si 15.37.

α-Chlorovinyltriethoxysilane (XIV). From 58 g of pyridine, 100 ml of benzene, 46 g of absolute ethyl alcohol, and 50 g of α-chlorovinyltrichlorosilane was obtained, as described in the preceding syntheses, α-chlorovinyltriethoxysilane, which began to decompose during distillation at atmospheric pressure.

Found %: C 42.89, 42.93: H 7.72, 7.74; Cl 15.46, 15.26; Si 12.54, 12.58. $C_8H_{17}O_3SiCl$. Calculated %: C 42.76; H 7.63; Cl 15.78: Si 12.49.

β-Chlorovinyltrimethoxysilane (XIII). From 30 g of methyl alcohol, 100 ml of benzene, 55 g of pyridine, and 47 g of β-chlorovinyltrichlorosilane [9], under the conditions described above, was obtained 18 g of (XIII).

Found %: C 32.80, 32.96. H 6.59, 6.62; Cl 18.88, 18.39; Si 15.57, 15.61. $C_5H_{11}O_3SiCl$. Calculated %: C 32.87; H 6.07; Cl 19.41; Si 15.37.

1-Chlorobutyn-2-oxy-4-dimethylethylsilane (XVI). From 100 g of ethyldimethylchlorosilane, 75 g of pyridine, 300 ml of ether, and 95 g of 1-chloro-2-butyn-4-ol [10] was obtained 60 g of (XVI).

Found %: C 50.21, 50.10; H 7.87, 7.96; Cl 18.87, 18.65; Si 14.33, 14.20. $C_8H_{15}OSiCl$. Calculated %: C 50.37; H 7.92: Cl 18.59; Si 14.71.

1-Chlorobutyn-2-oxy-4-trimethylsilane (XV) was similarly synthesized using the same proportions of reactants. 55 g was obtained.

Found %: C 47.51, 47.56; H 7.30, 7.33; Cl 20.16, 20.41; Si 15.67, 16.20. $C_7H_{13}OSiCl$. Calculated %: C 47.59, H 7.36; Cl 20.09; Si 15.90.

Condensation of $(C_2H_5)_2SiCl_2$ with sodium. 46 g of sodium was finely divided by stirring in 300 ml of boiling toluene. After cooling, 3 ml of ethyl acetate was added to the flask, and 78.5 g of diethyldichlorosilane was added with stirring over a period of 40 minutes in a manner such that the temperature did not rise above 50°. The contents of the flask were then refluxed for 2 hours and then allowed to stand overnight. The precipitate was then filtered and washed with fresh ether. After distillation of the ether, distillation of the 41 g of liquid residue gave four fractions: 1st, 70-114° (4 mm), 10%; 2nd, 114-175° (4 mm), 34%; 3rd, 175-240° (4 mm) 25%; 4th, >240° (4 mm), 31 . Upon a second distillation the distillate contained materials with molecular weights of from 370 to 1200. 150-155° fraction, mol. wt. 370, n_D^{20} 1.5022; 202-230° fraction (4 mm), mol. wt. ~400; fraction >240° (4 mm), mol. wt. 1200.

β-(Trimethylsilyl)isopropyl thioacetate (XVIII). 10 g of trimethylallylsilane and 48 g of thioacetic acid were mixed. After 5 minutes, the temperature had risen to ~65°, and after another 5 minutes, it began to drop. On the following day, vacuum distillation gave 14.5 g of (XVIII).

Found %: C 50.72, 50.58; H 9.33, 9.53; Si 14.81, 14.43; S 17.20. $C_8H_{18}OSSi$. Calculated %: C 50.47; H 9.53; Si 14.75; S 16.83.

SUMMARY

1. It was found that 1-chlorocyclohexene and α-chlorostyrene readily condense with $(CH_3)_3SiCl$, under the conditions of the Wurtz synthesis, forming trimethyl(1-cyclohexenyl)silane (X) and trimethyl-α-styrylsilane (VIII), respectively.

2. It was established that thioacetic acid adds to trimethylallylsilane with the evolution of heat.

3. Twelve unsaturated organosilicon compounds containing double and triple bonds, which have not been described in the literature, were prepared.

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STEREOCHEMISTRY OF THE BROMINATION OF ACETYLENIC ALCOHOLS

I. N. Nazarov and L. D. Bergelson

Data on the stereochemistry of the addition of halogens to a triple bond are few and contradictory. It is known that chlorine adds to acetylene with the formation of a mixture of cis- and trans-dichloroethylenes [1]. Bromination of tetrolic acid in chloroform and in the dark leads chiefly to the formation of the cis-dibromo acid, but in the sunlight the trans-isomer is the main product [2-4]. Propiolic acid behaves differently: in chloroform in the sunlight, the cis-dibromo acid is formed, while in the dark the product is a mixture of the cis- and trans-isomers [5, 6]. Bromination of phenylpropiolic [3, 4, 7, 8], p-nitropropiolic [9], and p-bromopropiolic [10, 11] acids in acetic acid or in chloroform leads to a mixture of the cis- and trans-dibromides. Dibromofumaric acid is the predominant product of the bromination of acetylenedicarboxylic acid in an aqueous medium [12-14]. Bromination of an ester of acetylenedicarboxylic acid in polar solvents leads to a mixture of dibromofumaric and dibromomaleic esters [15]. Only the dibromofumaric ester is formed in the presence of lithium bromide. Trans-dihalostilbenes are the chief products of the chlorination and bromination of tolane in ether [16]. Chlorination of hexyne in polar solvents leads chiefly to the trans-addition product [17].

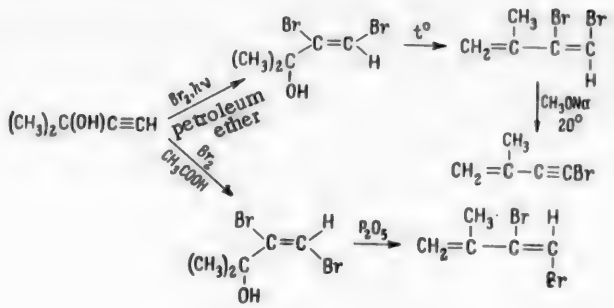
The halogenation of acetylenic alcohols has been studied still less. By chlorination of dimethylethynylcarbinol in carbon tetrachloride and in methanol, Hennion and Wolf [18] obtained two isomeric dichlorides, and they considered a priori that the trans-dichloride was the product in the first case and the cis-isomer in the second. There are, however, indirect data which indicate that the cis-derivative is predominately formed during the halogenation of acetylenic alcohols in a non-polar medium. Thus, from the bromination of tetramethyl- and tetraphenylbutynediol in chloroform, A. A. Kruglov [19] isolated furan derivatives, which correspond to the cis-dibromo glycols. A similar result was obtained from the bromination of tetramethylbutynediol in carbon tetrachloride [18].

In the present work, we studied the stereochemistry of the bromination of dimethylethynylcarbinol and 1-ethynylcyclohexanol. Bromination of these acetylenic alcohols was carried out both in a polar solvent (in aqueous acetic acid) and in a non-polar medium (in petroleum ether, with irradiation and in the presence of benzoyl-perioxide). In the latter case, the bromination reaction apparently proceeded chiefly by a radical mechanism, since it is sharply suppressed in the dark. We found that the reaction could be directed toward the formation of the cis- or of the trans-dibromovinylcarbinol depending on the bromination conditions. The purity of the liquid stereoisomers was verified by conversion of them to the p-nitrobenzoates and saponification of the latter; the product was considered pure only when the constants of the original alcohol and those of the product of the saponification of the p-nitrobenzoate were in agreement.

Bromination of the dimethylethynylcarbinol in aqueous acetic acid proceeds stereospecifically and leads to the formation of the trans-dibromovinyldimethylcarbinol. Photochemical bromination in petroleum ether gives chiefly the cis-dibromovinyldimethylcarbinol, but there was also formed a small amount of the trans-isomer and also some cis-3, 4-dibromoisoprene, which is formed as a result of dehydration of the cis-dibromovinyl alcohol. The configurations of the cis- and trans-dibromovinyldimethylcarbinols were confirmed by two independent routes: 1) in the infrared spectrum of the trans-dibromovinyldimethylcarbinol there was an intense band of out-of-plane vibrations (at 980 cm^{-1}*), which is characteristic of transolefins. This band was practically absent in the spectrum of the cis-isomer. The band characteristic of valence vibrations of the double bond was shifted toward the ultraviolet region in the case of the cis-isomer (1488 cm^{-1} for the trans-dibromide and 1502 cm^{-1} for the cis-isomer).

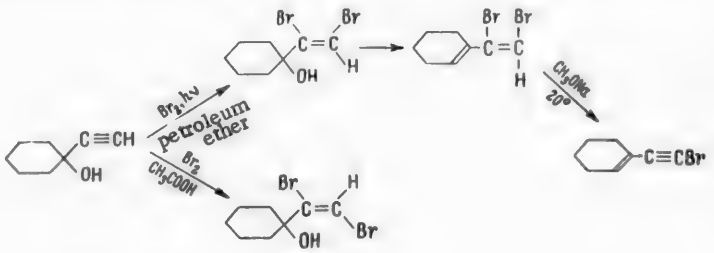
* The infrared spectra were taken in chloroform.

2) In contrast to the trans-isomer, cis-dibromovinyldimethylcarbinol is not very stable, and partially dehydrates just on standing in a desiccator over phosphorus pentoxide. It is practically completely converted to cis-3, 4-dibromoisoprene on distillation under a vacuum of 20 mm. The trans-isomer remains unchanged under these conditions, and is dehydrated only on distillation with a dehydration agent, forming trans-3, 4-dibromoisoprene. The cis- and trans-dibromoisoprenes are sharply differentiated by their behavior toward alkali. While the cis-isomer splits out hydrogen bromide in the presence of sodium methylate in the cold, being converted to isopropenylbromoacetylene, trans-dibromoisoprene remains practically unchanged under these conditions. Since dehydrobromination in alkaline medium proceeds by an E2 mechanism, i. e., with trans-removal of the elements of hydrogen bromide [20], these data are in good agreement with the proposed configurations of the dibromovinyldimethylcarbinols.



In 1943, A. A. Petrov [21] reported the photochemical bromination of dimethylethynylcarbinol in chloroform, but did not determine the geometrical configurations of the resulting dibromo alcohols. Judging from our data, his product was the incompletely purified trans-isomer. By dehydration of this mixture, Petrov obtained the stereoisomeric 3, 4-dibromoisoprenes, the constants of which satisfactorily agree with the constants of our cis- and trans-dibromodienes.

The bromination of 1-ethynylcyclohexanol proceeds in a completely analogous manner. In aqueous acetic acid, the basic product is the liquid trans-1-(dibromovinyl)cyclohexanol, which was obtained previously in our laboratory by treatment of ethynylcyclohexanol with N-bromo-acetamide [22]; in the light in petroleum ether, the chief product of the reaction is the crystalline cis-isomer with a m. p. of 72-73° [23]. The infrared spectra of the cis- and trans-dibromovinylcyclohexanols agree with the spectra of the stereoisomeric dibromovinyldimethylcarbinols (intense bands at 982 and 1484 cm^{-1} for the trans-isomer and a band at 1501 cm^{-1} for the cis-isomer).

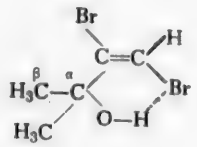


As does its acyclic analog, cis-dibromovinylcyclohexanol, in contrast to the trans-isomer, dehydrates on distillation under vacuum. The resulting cis-dibromovinyl-1-cyclohexene reacts in the cold with sodium methylate, being converted in good yield to cyclohexenylbromoacetylene.

Isopropenyl- and cyclohexenylbromacetylenes are not distillable at atmospheric pressure, and in the air, they darken after several minutes. Their structures were proved by hydrolysis by boiling with a solution of alkali in aqueous methanol. The hydrolysis of the first gave dimethylacrylic acid in good yield, while the second was converted by hydrolysis to cyclohexenylacetic acid.

On heating with alcoholic alkali, the aliphatic acetylenic bromides, in contrast to phenylbromoacetylene, are converted to acetylenes [24]. Vinyl acetylenic bromides behave, under these conditions, just as phenylbromoacetylene does. Thus, the presence of a vinyl group in a position conjugated with the triple bond imparts a positive character to the acetylenic bromine. An attempt to carry out the dehydrobromination of cis-dibromovinylcarbinols was unsuccessful, since they split out bromoacetylene at an elevated temperature in an alkaline medium.

It is interesting to note that the ease of dehydration of cis- and trans-dibromovinyl alcohols varies in opposite directions depending on the reaction conditions. Only the cis-dibromides are dehydrated during pyrolysis, and this occurs under exceptionally mild conditions. On heating the stereoisomeric dibromovinyldimethylcarbinols with acetic anhydride in the presence of sulfuric acid, only the trans-isomer is dehydrated, while the cis-dibromocarbinol is acetylated. It is well known that pyrolytic reactions involving the splitting out of a molecule are cis-elimination reactions, the four reaction centers in the transition state being located in the same plane [23]. It is probable that the hydroxyl group of the trans-isomer cannot be disposed in the same plane with the remaining three reaction centers (the α- and β-carbon atoms and one of the β-hydrogen atoms) owing to the formation of a hydrogen bond with the bromine.



Cis-dibromovinylcarbinols are not converted to the trans-isomers under the conditions under which the latter are formed, i. e., in acetic acid solution in the presence of traces of bromine. Apparently, the interaction of acetylenic alcohols with bromine proceeds by different mechanisms in polar and non-polar media; one of our succeeding communications will be devoted to this subject.

EXPERIMENTAL

Preparation of trans-dibromovinyldimethylcarbinol. A solution of 82 g of bromine in 100 ml of 70% acetic acid was added dropwise and with stirring at 20-25° to a solution of 42 g of dimethylethynylcarbinol in 150 ml of 70% aqueous acetic acid containing 0.5 g of potassium bromide. The bromination was accompanied by the liberation of heat (cooled with cold water), and was complete after 2 hours. To the solution was added 150 ml of water, the oil which separated was removed, the aqueous layer extracted with ether, the combined ethereal solutions washed with water, a saturated solution of sodium bicarbonate, a saturated solution of sodium hyposulfite, and again with water, dried with magnesium sulfate, and fractionated by means of a dephlegmator. After two-fold distillation under vacuum, 90.6 g of trans-dibromovinyldimethylcarbinol was obtained in the form of a colorless liquid with a weak lachrymatory effect.

B.p. 76.5-77° at 7 mm, n_D^{20} 1.5469, d_4^{20} 1.855, MR_D 41.70; calc. 41.88. Found %: C 24.56, 24.34; H 3.21, 3.24; Br 65.36, 65.49. $C_5H_8OBr_2$. Calculated %: C 24.62; H 3.30; Br 65.54.

2.5 g of trans-dibromovinyldimethylcarbinol and 1.7 g of p-nitrobenzoyl chloride in 10 ml of dry pyridine were allowed to stand for 24 hours at room temperature. The pyridine hydrochloride was filtered, 50 ml of ether was added to the filtrate, the mixture was extracted with 10% hydrochloric acid, with a saturated solution of soda, then with water, and the remaining mixture was then dried with magnesium sulfate. After distillation of 40 ml of ether, precipitation of crystals of the p-nitrobenzoate began. 20 ml of petroleum ether (b. p. 40-50°) was added, and the p-nitrobenzoate of trans-dibromovinyldimethylcarbinol, m. p. 119.2-119.4°, was obtained by recrystallization from the mixture of petroleum ether and ether (2:1).

Found %: C 36.23, 36.28; H 2.71, 2.83; Br 40.73, 40.59. $C_{12}H_{11}O_4NBr_2$. Calculated %: C 36.66; H 2.82; Br 40.67.

Saponification of the p-nitrobenzoate with a solution of potassium hydroxide in 20% aqueous alcohol (24 hours at room temperature) gave the original carbinol with a b. p. of 76.5-77° (7 mm), n_D^{20} 1.5465.

Preparation of trans-1-(dibromovinyl)cyclohexanol. 6.2 g of ethynylcyclohexanol in 40 ml of 70% acetic acid was brominated under the conditions indicated above using 8 g of bromine in 20 ml of glacial acetic acid. Fractional distillation gave 10.1 g of trans-1-(dibromovinyl)cyclohexanol in the form of a colorless liquid with a b. p. of 107-109° (2.5 mm), $n_D^{18.5}$ 1.5684 [22]. The p-nitrobenzoate of trans-1-(dibromovinyl)cyclohexanol was obtained in the form of slightly yellow needles melting at 153.2-154° (from a mixture of petroleum ether and ether, 2:1).

Found %: C 41.68, 41.77; H 3.63, 3.62; Br 36.91, 37.04. $C_{15}H_{15}O_4NBr_2$. Calculated %: C 41.91; H 3.49; Br 36.93.

Saponification of the p-nitrobenzoate with a solution of potassium hydroxide in 20% aqueous alcohol (40 hours at room temperature) led to the original carbinol with $n_D^{19.5}$ 1.5680.

Preparation of cis-dibromovinyldimethylcarbinol and cis-3, 4-dibromoisoprene. To a solution of 42 g of dimethylethynylcarbinol and 0.2 g of benzoyl peroxide in 150 ml of petroleum ether (b. p. 50-60°) was added, with stirring and irradiation (300 W), 82 g of bromine in 100 ml of petroleum ether, the rate of addition being controlled so that the temperature of the reaction mixture did not exceed 35°. The bromination required about 2 hours. The product was washed with water, a solution of hyposulfite, again with water, and dried with magnesium sulfate. Fractional distillation under vacuum, first with a dephlegmator and then in a column, gave the following fractions: 1st, 8.8 g of cis-3, 4-dibromoisoprene in the form of a yellow-green liquid:

B.p. 53.6-55° (6 mm), n_D^{20} 1.5662, d_4^{20} 1.828, MR_D 40.31; calc. 39.89, EM_D 0.42. Found %: C 26.58, 26.64; H 2.87, 2.83. $C_5H_6Br_2$. Calculated %: C 26.84; H 2.71.

On standing in the light for several days, the substance thickened without darkening. It darkened on long standing. It can be stored without change for 30 days in the dark at +2° in the presence of hydroquinone; 2nd, 5.1 g of trans-dibromovinyldimethylcarbinol with a b. p. of 76.4-77.6° (7 mm), $n_D^{20.5}$ 1.5458 (contained a certain amount of the cis-isomer). After 4-fold recrystallization from a mixture of ether and petroleum ether (1:2), the p-nitrobenzoate of this fraction melted at 119-119.5°, and a mixture with the above-described p-nitrobenzoate of trans-dibromovinyldimethylcarbinol showed no melting point depression; 3rd, 60.7 g of cis-dibromovinyldimethylcarbinol:

B.p. 79-80° (6 mm), n_D^{20} 1.5416, d_4^{20} 1.845, MR_D 41.60; calc. 41.88. Found %: C 24.84, 24.73; H 3.29, 3.36. $C_5H_8OBr_2$. Calculated %: C 24.62; H 3.30.

After 3-fold recrystallization from a mixture of petroleum ether and ether, the p-nitrobenzoate of cis-dibromovinyldimethylcarbinol melted at 101-102° (yellow needles). A mixed sample with the p-nitrobenzoate of the trans-isomer (m. p. 119.2-119.4°) melted at 80°.

Found %: C 36.57, 36.73; H 2.88, 2.89; Br 40.78, 40.65. $C_{12}H_{11}O_4NBr_2$. Calculated %: C 36.66; H 2.82 Br 40.67.

On saponification of this p-nitrobenzoate with a solution of potassium hydroxide in 20% aqueous alcohol at room temperature, the original cis-carbinol was obtained with a b. p. of 79-80° (6 mm), n_D^{20} 1.5413. Cis-dibromovinyldimethylcarbinol is a slightly yellow, viscous liquid with a rather sharp lachrymatory effect; it darkens on standing. Distillation of the carbinol under vacuum (20 mm) always liberated water and formed cis-3, 4-dibromoisoprene (about 10% of the weight of the carbinol).

Preparation of cis-1-(dibromovinyl)cyclohexanol. 6.2 g of 1-vinylcyclohexanol in 40 ml of petroleum ether (b. p. 40-60°) was brominated, as described above, in the presence of 0.3 g of benzoyl peroxide using 8 g of bromine in 50 ml of petroleum ether. The bromination proceeded comparatively slowly, and required about 3 hours. The reaction mixture was washed with water, with a solution of hyposulfite, again with water, and dried with magnesium sulfate. After distillation of 30 ml of solvent under vacuum, 12.1 g of cis-1-(dibromovinyl)cyclohexanol precipitated in the form of colorless crystals melting at 72-73° [22] after 3-fold recrystallization from a mixture of ether and petroleum ether 1:2).

The cis-carbinol partially dehydrated on standing in a desiccator over phosphorus pentoxide. The cis-carbinol did not give a p-nitrobenzoate on standing for a period of 4 days in pyridine medium.

Acetylation of cis-dibromovinyldimethylcarbinol. 20 g of cis-dibromovinyldimethylcarbinol was added, with stirring, to a mixture of 50 ml of acetic anhydride and 3 ml of concentrated sulfuric acid, and the mixture was heated for 6 hours at 70° 150 ml of ether was added to the mixture, and the mixture was washed with water and then with a saturated solution of sodium bicarbonate, and dried with calcium chloride. Vacuum distillation gave 18.5 g of the acetate of cis-dibromovinyldimethylcarbinol:

B.p. 84-86° (9 mm), n_D^{17} 1.5180, n_D^{20} 1.5172, d_4^{20} 1.671, MR_D 48.89; calc. 49.03 Found %: C 29.20, 29.23; H 3.48; 3.44; Br 55.70, 55.95. $C_7H_{10}OBr_2$. Calculated %: C 29.40; H 3.52; Br 55.89.

This same result was obtained by treatment of 20 g of cis-dibromovinyldimethylcarbinol at a temperature not above 10° with 25 ml of acetic anhydride containing 3 drops of concentrated sulfuric acid.

Dehydration of trans-dibromovinyldimethylcarbinol. 25 g of trans-dibromovinyldimethylcarbinol was added dropwise to 15 g of phosphorus pentoxide contained in a Claisen flask in which a vacuum of 20 mm was maintained. A vigorous reaction began after 5 minutes (after the additon of 5 ml of the carbinol). Owing to the heat of the reaction, a liquid with a b. p. of about 65° (20 mm) began to distill. The addition of the carbinol was continued at a rate such that uniform boiling of the mixture was maintained. The reaction mixture was then heated at 80-90°, distilling the reaction product completely. Distillation of the reaction product at 7 mm gave the following fractions: 1st, trans-3, 4-dibromoisoprene, yield 10.6 g:

B. p. 41-43.5° (7 mm), n_D^{20} 1.5473, d_4^{20} 1.7805, MR_D 40.25; calc. 39.89, EM_D 0.36. Found %: C 26.69, 26.67; H 2.42, 2.55; Br 70.40, 70.56. $C_5H_6Br_2$. Calculated %: C 26.84, H 2.71; Br 70.45.

2nd, cis-3, 4-dibromoisoprene, yield 2.95 g, b. p. 53-55° (7 mm), $n_D^{18.5}$ 1.5662. b) 20 g of trans-dibromovinyldimethylcarbinol was rapidly added to a mixture of 50 ml of acetic anhydride and 3 ml of concentrated sulfuric acid (the temperature of the mixture increased from 20 to 50°), and the mixture was heated for 3 hours at 60-70°. After the usual treatment, trans-3, 4-dibromoisoprene was obtained in a yield of 14.1 g, b. p. 42.5-44° (7 mm), n_D^{20} 1.5479.

Dehydration of cis-dibromovinyldimethylcarbinol. 12 g of unpurified dimethylethynylcarbinol was brominated in petroleum ether, as indicated above (see preparation of cis-dibromovinyldimethylcarbinol), and the reaction product was distilled at 20 mm. The distillation was accompanied by the splitting out of water (temperature of the vapors was 72-80°). The distillate was dried with magnesium sulfate, and distilled a second time. There were obtained 17.5 g of cis-3, 4-dibromoisoprene, b. p. 54-55.5° (6.5 mm), $n_D^{19.5}$ 1.5663, and 8.3 g of a fraction with a b. p. of 55-70°, which contained cis-3, 4-dibromoisoprene along with the original carbinol. Residue 2.5 g.

Preparation of isopropenylbromoacetylene. 25 g of cis-3, 4-dibromoisoprene (n_D^{20} 1.5660) was added to a solution of sodium methylate prepared from 5.2 g of sodium and 100 ml of methanol. The mixture was heated at 30° for 30 minutes, whereupon a voluminous precipitate of sodium bromide (about 10 g) was formed. On the following day, 150 ml of ether and 100 ml of water were added to the mixture. The ether layer was washed with water, 10% hydrochloric acid, again with water, dried with calcium chloride, and distilled under vacuum in an atmosphere of nitrogen. 8.2 g of isopropenylbromoacetylene was obtained in the form of a mobile liquid with a sharp odor; the liquid darkened on standing in the light for several minutes.

B.p. 41-43° (68-70 mm), n_D^{20} 1.5076. Found %: C 41.86, 42.09; H 3.61, 3.58; Br 55.67, 55.02. C_5H_5Br. Calculated %: C 41.42; H 3.48; Br 55.12.

10 g of trans-3, 4-dibromoisoprene was practically unchanged under the same conditions (after the treatment, 7.3 of unchanged trans-dibromide was recovered, b. p. 41-44° at 7 mm, n_D^{20} 1.5469).

Conversion of isopropenylbromoacetylene to β, β-dimethylacrylic acid. 3.4 g of isopropenylbromoacetylene was refluxed for 12 hours with a solution of sodium methylate prepared from 2 g of sodium, 50 ml of methanol, and 30 ml of water. The methanol was distilled under vacuum, and the residue was extracted with ether (Solution A). The aqueous layer was acidified with 10% hydrochloric acid, extracted with ether, the ether layer washed with water, and the ether distilled under vacuum. The semi-crystalline precipitate was distilled at 20 mm, and the product was recrystallized from water containing 5% methanol. 2.2 g of β, β-dimethylacrylic acid was obtained with a m. p. of 69-70°. From Solution A, after drying with calcium chloride and distillation of the ether, was obtained a small amount of undistillable and uncrystallizable tar.

Preparation of cis-dibromovinyl-1-cyclohexene. Unpurified cis-1-(dibromovinyl)cyclohexanol, prepared under the conditions indicated above from 10.3 g of ethynylcyclohexanol, was distilled at 8 mm. When the temperature of the liquid reached 135°, splitting out of water began, and along with the water, was distilled at first a dark liquid with a b. p. of 120-130° at 8 mm (about 6g) and then a fraction with a b. p. of 130-135° at 8 mm (13 g). This fraction was dried with calcium chloride, and distilled at 1.5 mm. After two distillations, 9.4 g of cis-dibromovinyl-1-cyclohexene was obtained in the form of a light yellow liquid, which darkened rapidly on standing in air.

B. p. 93-94° at 5 mm, n_D^{21} 1.5856, d_4^{21} 1.722, MR_D 51.86; calc. 51.54, EM_D 0.32. Found %: C 36.43, 36.32; H 3.84, 3.89. $C_8H_{10}Br_2$. Calculated %: C 36.10; H 3.80.

Preparation of 1-cyclohexenylacetic acid. 9 g of cis-dibromovinyl-1-cyclohexene and a solution of sodium methylate, prepared from 4 g of sodium and 250 ml of methanol, was allowed to stand overnight at room temperature. On the following morning, a solution of 5 g of sodium hydroxide in 50 ml of water was added to the reaction mixture, which consisted of a dark liquid and a precipitate of sodium bromide, and the mixture was refluxed for 20 hours. After the usual treatment, 5.3 g of an acid fraction was obtained, and this was distilled at 140-150° (1.5 mm). The solidified distillate was recrystallized twice from water containing 5% methanol, and 4.5 g of 1-cyclohexenylacetic acid, m. p. 37-38°, was obtained. From the mother liquor, after concentration, was obtained 0.35 g of cyclohexylidenacetic acid with a m. p. of 90-91° (from water).

SUMMARY

Partial bromination of acetylenic alcohols in an aqueous solution of acetic acid leads to the formation of trans-dibromovinylcarbinols, while cis-dibromovinylcarbinols are formed in petroleum ether under the influence of light in the presence of benzoyl peroxide. The dehydration of cis- and trans-dibromovinylcarbinols to the corresponding dibromodienes is described. The cis-form of the latter readily splits out hydrogen bromide under the influence of sodium methylate, and is converted to a vinylbromoacetylene, which, on heating with a solution of alkali, gives a high yield of an acid of the acrylic acid series or of the type of vinylacetic acid.

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2, 2'-BIPHENYLENEHALONIUM SALTS

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By means of the heterolytic decomposition of diazonium fluoborates in a medium of chloro- or bromobenzene, we accomplished the synthesis of a number of diarylchloronium and diarylbromonium salts [1]. With the aim of comparing these compounds with the biphenylenebromonium and biphenylenechloronium salts obtained by Sandin and Hay [2], we used the method of these authors to prepare a number of new 2, 2'-biphenylenehalonium salts, which are described in this article. These heterocyclic aromatic halonium salts are considerably more thermally stable and less soluble than our diarylbromonium and diarylchloronium salts with the corresponding anions.

EXPERIMENTAL

The 2, 2'-biphenylenebromonium and 2, 2'-biphenylenechloronium salts were prepared as follows. o-Iodonitrobenzene [3] was prepared from o-nitroaniline, and the former was converted to 2, 2'-dinitrobiphenyl by the action of copper powder [4]. The 2, 2'-dinitrobiphenyl was reduced with tin and hydrochloric acid to 2, 2'-diaminobiphenyl [5], one of the amino groups of which was protected by acylation [4], and the other was then replaced by bromine or chlorine by means of the Sandmeyer reaction. The acetyl group was then removed by boiling with alcoholic HCl, and the resulting 2-bromo- (or, correspondingly, 2-chloro-) 2' aminobiphenyl was diazotized. Subsequent heating of the resulting diazonium salt led to the formation of 2, 2'-biphenylenechloronium or 2, 2'-biphenylenebromonium chloride [2].

Biphenylenebromonium and biphenylenechloronium salts having other anions were prepared by mixing solutions of salts having the desired anions with concentrated solutions of biphenylenebromonium chloride or biphenylenechloronium iodide.

2, 2'-Biphenylenebromonium salts. 1. Biphenylenebromonium chloride was obtained in the form of white crystals with a m. p. of 205-207° [2], readily soluble in methyl and ethyl alcohols, nitrobenzene, and hot water and insoluble in ether, benzene, chloroform, ethyl acetate, and acetone (Figure 1)*.

2. Biphenylenebromonium bromide was prepared from 0.2 g of biphenylenebromonium chloride and 0.09 g of potassium bromide. The yield was 0.08 g. After recrystallization from ethyl alcohol, the salt had a decomposition temperature of 194-194.5°, and was in the form of white needles, very soluble in cold water and ethyl and methyl alcohols and insoluble in ether (Figure 2).

Found %: C 46.04, 45.97; H 2.64, 2.57; Br 51.28, 51.58. $C_{12}H_8Br_2$. Calculated %: C 46.18; H 2.58; Br 51.22.

3. Biphenylenebromonium thiocyanate was prepared from a concentrated solution of 0.2 g of biphenylenebromonium chloride and a saturated solution of potassium thiocyanate. The yield was 0.17 g; the white crystals, which turned slightly rose-colored on standing, were readily soluble in hot ethyl alcohol and insoluble in ether. After two recrystallizations from alcohol, the decomposition temperature was 147.5-148.5°.

Found %: C 54.03, 53.97; H 2.37, 2.43; N 5.13, 5.10. $C_{13}H_8NSBr$. Calculated %: C 53.79; H 2.71; N 4.83.

4. Biphenylenebromonium fluoborate was precipitated from a concentrated solution of biphenylenebromonium chloride by the addition of excess sodium fluoborate. The yield was 0.21 g; the fluoborate was in the form of white crystals with a decomposition temperature of 199.5-200°, very soluble in warm water and in cold methyl and ethyl alcohols and insoluble in ether. The salt was purified by two-fold reprecipitation from anhydrous methyl alcohol with absolute ether.

* The absorption spectra were obtained in the Optical Laboratory of the Institute of Heteroorganic Compounds using a V. I. Dianova-Klokov FP-1 spectrophotometer. For reference, the spectrum of a mercury lamp is shown along the horizontal axis of the figures.

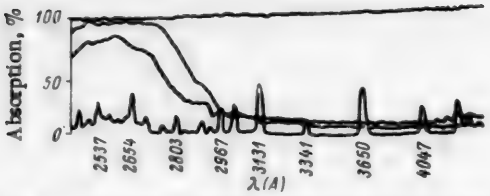

Fig. 1. Absorption spectrum of biphenylenebromonium chloride. Solvent CH_3OH; molar concentration $3 \cdot 10^{-4}$. λ_{max} 2890 A (ϵ_{max} $0.22 \cdot 10^4$); 2700 A (ϵ_{max} $1.89 \cdot 10^4$); 2590 A (ϵ_{max} $2.56 \cdot 10^4$); 2520 A (ϵ_{max} $2.33 \cdot 10^4$). (NaCl does not absorb in this region of the spectrum).

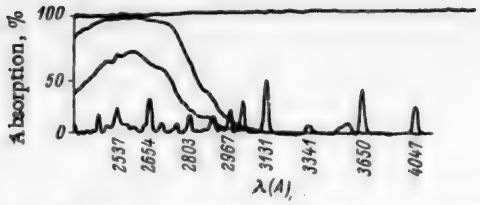

Fig. 2. Absorption spectrum of biphenylenebromonium bromide. Solvent CH_3OH; molar concentration $3 \cdot 10^{-4}$. λ_{max} 2880 A (ϵ_{max} $1.3 \cdot 10^4$); 2600 A (ϵ_{max} $1.8 \cdot 10^4$); 2510 A (ϵ_{max} $1.6 \cdot 10^4$). NaBr does not absorb in this region of the spectrum).

Found %: C 45.47, 45.55; H 2.70, 2.59. $C_{12}H_8BrBF_4$. Calculated %: C 45.20; H 2.53.

5. Biphenylenebromonium picrate was prepared from 0.2 g of biphenylenebromonium chloride and 0.18 g of picric acid. The yield was 0.1 g; the lemon-yellow crystals were difficultly soluble in water, ethyl alcohol, and acetone, insoluble in ether, chloroform, and ethyl acetate, and readily soluble in nitrobenzene. After two recrystallizations from alcohol, the decomposition temperature was 173.5-174.5°.

Found %: C 46.98, 46.83; H 2.43, 2.50; Br 16.99, 16.80; N 9.22, 9.33. $C_{18}H_{10}O_7N_3Br$. Calculated %: C 46.98; H 2.20; Br 17.36; N 9.13.

6. Biphenylenebromonium ferricyanide was prepared by the addition of a saturated solution of potassium ferricyanide to a concentrated solution of 0.2 g of biphenylenebromonium chloride. The yield was 0.12 g; the greenish yellow crystals were moderately soluble in water and insoluble in the usual organic solvents. The salt, purified by recrystallization from water, decomposed at 198°.

Found %: C 55.04, 55.15; H 2.63, 2.73; Br 25.97, 26.45; Fe 6.61, 6.90. $C_{42}H_{24}N_6Br_3Fe$. Calculated %: C 55.52; H 2.66; Br 26.40; Fe 6.15.

7. Biphenylenebromonium nitroprusside was prepared from a concentrated solution of 0.2 g of biphenylenebromonium chloride and a concentrated solution of sodium nitroprusside. The yield was 0.11 g. The salt was purified by 2-fold reprecipitation from anhydrous methyl alcohol with absolute ether; it was in the form of dirty rose crystals, readily soluble in methyl alcohol, acetone, and hot water and insoluble in ether. The salt decomposed at 195-200° with intense blackening.

Found %: C 50.92, 50.67; H 2.49, 2.37. $C_{29}H_{16}ON_6Br_2Fe$. Calculated %: C 51.22; H 2.37.

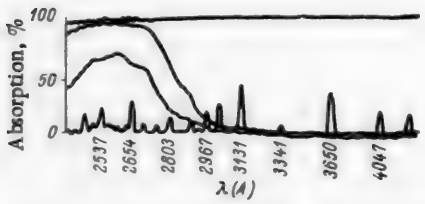

Fig. 3. Absorption spectrum of biphenylenebromonium fluoborate. Solvent CH_3OH; molar concentration $3 \cdot 10^{-4}$. λ_{max} 2890, 2680 A (ϵ_{max} $1.3 \cdot 10^4$); 2600 A (ϵ_{max} $1.7 \cdot 10^4$); 2520 A (ϵ_{max} $1.5 \cdot 10^4$). ($NaBF_4$ does not absorb in this region of the spectrum).

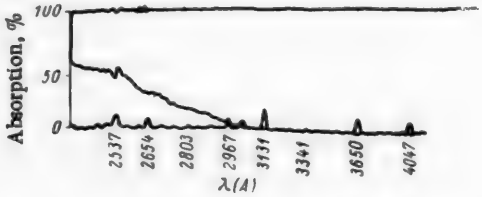

Fig. 4. Absorption spectrum of biphenylenebromonium iodide. Solvent CH_3OH; molar concentration $1 \cdot 10^{-4}$. λ_{max} 2570, 2680 A (KI does not absorb in this region of the spectrum).

8. Biphenylenebromonium dichromate was prepared by the addition of a solution of potassium dichromate (to complete precipitation) to 80 ml of a cold, saturated solution of biphenylenebromonium chloride. The yield was 0.24 g; the orange crystals were moderately soluble in hot water, practically insoluble in methyl and ethyl alcohols, ether, and dioxane. After 2-fold recrystallization from water, the salt had a decomposition temperature of 135-136°.

Found %: C 42.57, 42.42; H 2.43, 2.45; Cr 15.03. $C_{24}H_{16}O_6Br_2Cr_2$. Calculated %: C 42.36; H 2.37; Cr 15.29.

9. Biphenylenebromonium chloroplatinate was prepared under the conditions of the preceding experiment from 90 ml of a saturated solution of biphenylenebromonium chloride and a solution of platinic chloride in 10% hydrochloric acid. The yield was quantitative; the light orange crystals were insoluble in water and the usual organic solvents. The salt, recrystallized from 10% hydrochloric acid, had a decomposition temperature of 209-210°.

Found %: C 33.39, 33.27; H 1.74, 1.68; Pt 21.93, 22.01. $C_{24}H_{16}Cl_6Br_2Pt$. Calculated %: C 33.05; H 1.85; Pt 22.38.

10. Biphenylenebromonium tetraphenylboron was precipitated by the addition of a saturated acetone solution of 0.23 g of potassium tetraphenylboron to an aqueous acetone solution of 0.2 g of biphenylenebromonium chloride. The yield was 0.2 g; the white, acicular needles were difficultly soluble in water and ethyl alcohol and insoluble in ether; after three-fold reprecipitation from acetone with absolute ether, the salt had a decomposition temperature of 200.5-201°.

Found %: C 78.70, 78.43; H 5.15, 5.33; B 2.12, 2.02; Br 14.81, 14.68. $C_{36}H_{28}BBr$. Calculated %: C 78.43; H 5.11; B 1.96; Br 14.50.

2, 2'-Biphenylenechloronium salts. 1. The biphenylenechloronium iodide was in the form of white crystals with a m. p. of 130.5-131.5° (after 2-fold reprecipitation from anhydrous methyl alcohol with absolute ether), readily soluble in cold methyl alcohol, ethyl alcohol, acetone, and nitrobenzene, insoluble in ether and the other ordinary organic solvents, and difficultly soluble in cold water. According to the data of reference [2]: m. p. 125-130° (Figure 4).

2. Biphenylenechloronium thiocyanate was prepared by the addition of solid potassium thiocyanate to a concentrated solution of 0.3 g of biphenylenechloronium iodide. The yield was 0.12 g; the fine colorless crystals, which turned rose-colored on standing, were soluble in methyl and ethyl alcohols, acetone, and nitromethane and insoluble in ether and benzene. The decomposition temperature was 98.5-99.5° after two reprecipitations from anhydrous methyl alcohol with absolute ether and from nitromethane with absolute ether (Figure 5).

Found %: N 5.92, 5.93. $C_{13}H_8NSCl$. Calculated %: N 5.70.

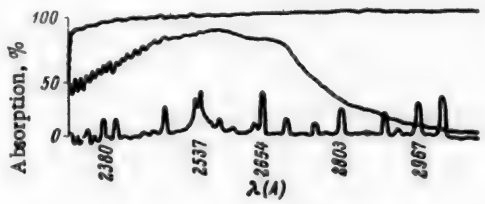

Fig. 5. Absorption spectrum of biphenylenechloronium thiocyanate. Solvent CH_3OH; molar concentration $6.8 \cdot 10^{-4}$. λ_{max} 2580, 2680 A (KCNS does not absorb in this region of the spectrum).

3. Biphenylenechloronium fluoborate was precipitated from a saturated solution of 0.27 g of biphenylenechloronium iodide with solid sodium fluoborate, of which an excess was used. The yield was 0.19 g; the colorless crystals were readily soluble in water, methyl alcohol, and nitromethane and insoluble in ether. The salt was purified by 2-fold reprecipitation from methyl alcohol with absolute ether. Decomposition temperature 169.5-170.5°.

Found %: C 51.99, 52.15; H 2.91, 2.96. $C_{12}H_8ClBF_4$ Calculated %: C 52.50; H 2.94.

4. Biphenylenechloronium tetraphenylboron was prepared from a saturated solution of 0.25 g of biphenylenechloronium iodide and a saturated aqueous solution of sodium tetraphenylboron with a yield of 0.22 g; the white acicular crystals had a decomposition temperature of 184-184.5° after 2-fold reprecipitation from acetone with absolute ether. The salt was readily soluble in acetone and nitromethane, difficultly soluble in water, and insoluble in ether.

Found %: C 84.74, 84.80; H 5.53, 5.52; B 2.10, 2.13. $C_{36}H_{28}BCl$. Calculated %: C 85.30; H 5.57; B 2.14.

5. Biphenylenechloronium nitroprusside was prepared by the addition of a concentrated solution of sodium nitroprusside to a saturated solution of 0.27 g of biphenylenechloronium iodide. The yield was 0.11 g; the fine, rose-colored crystals were readily soluble in water and methyl alcohol and insoluble in ether. After reprecipitation from methyl alcohol with absolute ether, the salt decomposed at about 260°.

Found %: N 14.17, 14.11; Fe 9.51, 9.39. $C_{29}H_{16}ON_6Cl_2Fe$. Calculated %: N 14.23; Fe 9.45.

6. Biphenylenechloronium picrate was prepared by the addition of a concentrated solution of picric acid to a saturated solution of 0.25 g of biphenylenechloronium iodide. The yield was 0.11 g; the light yellow acicular crystals were soluble in acetone, difficultly soluble in water, and insoluble in ether. After recrystallization from acetone, the salt had a decomposition temperature of 169.5-170.5°.

Found %: C 52.32, 52.17; H 2.59, 2.65; N 9.90, 9.90. $C_{18}H_{10}O_6N_3Cl$. Calculated %: C 52.02; H 2.42; N 10.14.

7. Biphenylenechloronium dichromate was prepared by the addition of a concentrated solution of potassium dichromate to a saturated solution of 0.26 g of biphenylenechloronium iodide. The yield was 0.12 g; the orange crystals were soluble in nitromethane and hot water and insoluble in ether. After recrystallization from water, the decomposition temperature was 138°.

Found %: C 48.21; H 2.52; Cr 17.87. $C_{24}H_{16}O_6Cl_2Cr_2$. Calculated %: C 48.74; H 2.73; Cr 17.59.

8. Biphenylenechloronium chloroplatinate was precipitated from a concentrated solution of biphenylenechloronium chloride by the addition of a concentrated solution of platinic chloride in 10% hydrochloric acid. The yield of the salt was quantitative; the fine, light orange crystals were soluble in 10% hydrochloric acid on heating and insoluble in water and methyl and ethyl alcohols. The salt, recrystallized from 10% hydrochloric acid, had a decomposition temperature of 180.5-181.5°.

Found %: C 36.69, 36.50; H 2.08, 2.08; Pt 24.62, 24.44. $C_{24}H_{16}Cl_6Pt$. Calculated %: C 36.79; H 2.06; Pt 24.92.

SUMMARY

For the purposes of comparison with the diarylbromonium and diarylchloronium salts previously prepared by us, the present paper describes the synthesis and certain properties of a number of new 2, 2'-biphenylenehalonium salts of the type first described by Sandin and Hay.

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THE ACETONATE OF 9, 10-DIHYDROXYSTEARIC ACID FROM ELAIDIC ACID. III

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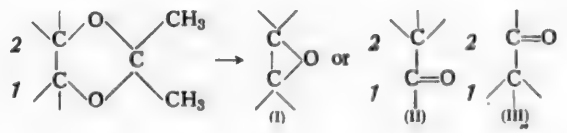
The acetonation method was proposed by one of us to determine the position of the hydroxyl groups in the diastereoisomeric 9, 10-dihydroxystearic acids [1], and somewhat later-in the 9, 10, 12-trihydroxystearic acids [2]. Recently G. V. Pigulevsky and I. L. Kuranova [3] used this method to determine the position of the OH and NH_2 groups in 9-amino-10-hydroxystearic acid, which they converted into the low-melting form of 9, 10-dihydroxystearic acid, giving the acetone derivative in high yield. As a result, the acetonation method proved to be valuable not only in determining the position of OH groups in cyclic diols [4], but also in aliphatic compounds, like the dihydroxy acids with the OH groups at some distance from the carboxyl.

A study of the effect of heat on the behavior of acetone derivatives (ketals) seemed worthwhile. In the decomposition of acetone derivatives it could be expected that either the α-oxide (I) or the isomeric keto compounds (II) and (III) would be formed.



In those cases where it was successful, this method could be used to go from olefins, through the glycols and their acetone derivatives (ketals), to α-oxides or oxo compounds.

In experiments made with the acetonate of 9, 10-dihydroxystearic acid obtained from elaidic acid we found that acetone, 10-ketostearic acid and tarry substances are formed in its decomposition. The maximum yield of 10-ketostearic acid reached 30%. This shows that it is possible to go from dihydroxy compounds, through their acetone derivatives, to keto compounds.

Together with the above, we determined the acid numbers of the acetonate of 9, 10-dihydroxystearic acid obtained from elaidic acid and isolated by the method described earlier [1]. When the acetonate was titrated directly with alcoholic KOH solution, its acid number was 117.7; after this stood for 1 hour at 15° with excess KOH solution, the acid number reached a limiting value of 131.5 and did not change on further standing. Only after it was heated for 2 hours with KOH solution did the acid number of the acetonate reach its theoretical value. Because of this, the acetonate was boiled for 4 hours with aqueous KOH solution to decompose any ester compounds. After such treatment we isolated 0.35 g of 9, 10-dihydroxystearic acid and 0.27 g of acetone from 20 g of the acetonate. The acetonate purified in this manner had its proper acid number of 157.4, which did not change after the acetonate had been stored for 2.5 months. These data show that the acetonation of 9, 10-dihydroxystearic acid is accompanied by side reactions, leading to an ester type of compound. However, the amount of this compound, if based on the yield of dihydroxystearic acid obtained in the alkaline treatment of the acetonate, is not sufficiently great to explain the substantial change in the acid number from 131.5 to 157.4. This problem, and also the reason for the change in the acid number of the acetonate at 15°, are to be the subject of a later investigation.

EXPERIMENTAL•

Twenty grams of 9, 10-dihydroxystearic acid with m. p. 95° was dissolved in 200 ml of 1% HCl solution in dry acetone and allowed to stand for 12 days at 15°. The method described in the paper [1] was used to isolate and purify the acetonation product from unreacted dihydroxystearic acid. The amount of unreacted dihydroxystearic acid was 0.8 g. The acetonation product had d_4^{20} 0.9524, n_D^{20} 1.4605. Determination of the acid number of the acetonate by direct titration with alcoholic KOH solution gave values of 117.71 and 117.76. The acid number of the acetonate after its alcohol solution was allowed to stand with 10 ml of alcoholic 0.1N KOH solution at 15° for 1 and 2 hours was 131.59 and 131.48, respectively, and after a weighed sample of the acetonate was heated at the boil for 2 hours with 10 ml of 0.1N alcoholic KOH solution it was equal to 153.94. The calculated acid number for $C_{21}H_{40}O_4$ is 157.37.

To remove substances of ester character from the acetonate, we took 20 g of the acetonation product with acid number 117.7 and treated it for 4 hours on a boiling water bath with 60 ml of 20% aqueous KOH solution in a flask, connected to a condenser fitted with an adapter, the end of which was immersed in a receiver containing distilled water. At the end of heating, the major portion of the liquid in the flask was distilled into the same receiver, and the amount of acetone in the distillate was determined by the Messinger method. The amount of acetone was 0.27 g. The residue in the flask, containing potassium salts, was dissolved in water and then carefully acidified in the cold with dilute hydrochloric acid. The deposited acetonate of 9, 10-dihydroxystearic acid was extracted with petroleum ether, after which this solution was washed with water until the test for Cl ion was negative, and then it was cooled to -20° to remove the free 9, 10-dihydroxystearic acid. This operation was repeated until the appearance of cloudiness was no longer observed when the cooled solution was allowed to stand for a long time. The solution was then dried over anhydrous Na_2SO_4. The residue remaining after vacuum-distillation of the petroleum ether was a clear, pale yellow, viscous oil:

d_4^{20} 0.9485, n_D^{20} 1.4565, MR_D 102.28; calc. 101.8

The acid numbers were determined for the acetonate obtained in this manner, as well as after 2.5-month storage: found: 157.36 and 156.22.

The acetonate with acid number 157.36 was heated in a metal bath for 1 and for 2 hours at 295-300°, and here weight losses of about 4.5% and 15%, respectively, were observed. The decomposition proceeds at a faster rate at 310-320°, and here the loss in weight after 1 hour was 18.9%, while at 330-336° it was already 20.2% in 30 minutes. In the decomposition of the acetonate the acetone, collected in the traps containing water, was determined by the iodoform reaction. The 10-ketostearic acid was isolated in the following manner from the acetonate decomposition products. The residue from the decomposition was treated with aqueous NaOH solution with heating, after which the solution was cooled and the Na salts filtered and decomposed with dilute hydrochloric acid. The viscous acids were melted on water until the test for chloride ion was negative, and then they were dissolved with heating in a water-alcohol (4:1) mixture. After this, the major portion of tarry products was removed by filtration and the filtrate, containing mainly 10-ketostearic acid, was evaporated. After drying in a desiccator the acid was recrystallized from carbon tetrachloride and from ethyl alcohol. It had m. p. 70-71°. The yield of 10-ketostearic acid in the above indicated experiments was: 8.9, 30.2 and 14.1%. The acid number of the 10-ketostearic acid was determined, proving to be equal to 183.83 and 185.03. For $C_{18}H_{34}O_3$ the acid number is 187.99.

We also prepared the oxime of the acid obtained by the Baruch method [5], which was obtained as an exceedingly viscous yellow oil.

Found%: N 4.64. $C_{18}H_{35}O_3N$. Calculated %: N 4.47.

Experiments on the decomposition of the acetonate of 9, 10-dihydroxystearic acid in vacuo at 50 and 100 mm, with distillation of the major portion of the substances, revealed that here a motley mixture of various acids and tarry products is formed.

• With the assistance of A. A. Maksimova.

SUMMARY

1. It was shown that the thermal decomposition of the acetonate of 9, 10-dihydroxystearic acid, obtained from elaidic acid, yields 10-ketostearic acid in 30% yield.

2. It was shown that the acetonation of 9, 10-dihydroxystearic acid gives, besides the ketal, also a small amount of ester-type substances, formed as the result of secondary reaction.

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CHEMISTRY OF HETEROCYCLES

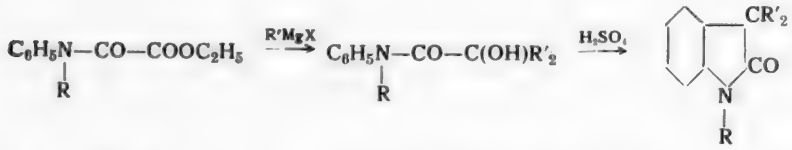
XXIX. N-ALKYL DERIVATIVES OF 3, 3-DIARYLOXINDOLES

P. A. Petyunin, V. S. Shklyaev and A. S. Pesis

To expand the method for the preparation of heterocyclic compounds based on arylamides of hydroxycarboxylic acids we synthesized some N-alkyl derivatives of the 3, 3-diaryloxindoles. In doing this we found it necessary to develop a convenient method for the preparation of the N-alkylated arylamides of α-hydroxycarboxylic acids. According to the literature these compounds are obtained by the reaction of organomagnesium compounds with the N-alkylated arylamides of benzoylformic acid [1]. However, due to the scarcity of the latter compounds, this method can have only limited application.

It was established by us that the N-alkylated arylamides of α-hydroxycarboxylic acids (IV—IX) can be obtained in good yields by the reaction of organomagnesium compounds with the N-alkyl derivatives of oxanilic ester (I—III). The latter are synthesized by the reaction of N-alkylanilines with ethoxalyl chloride in either dry ether or pyridine medium. The advantage of our method is that it is more accessible and can be used to obtain extremely different N-alkyl derivatives of the α-hydroxycarboxylic acid arylamides. When treated with concentrated sulfuric acid the N-alkylarylamides (IV—IX) are very easily converted in high yields into the N-alkyl derivatives of 3, 3-diaryloxindoles (X—XV). The reaction goes through the stage of forming a halochromic salt, and the oxindole ring cyclizes into a halochromic cation [2].

As is known, the arylamides of hydroxycarboxylic acids show basic properties when compared to the acids [2]. In this connection it is interesting to mention that the basic properties increase substantially in going from the arylamides to their N-alkyl derivatives. Thus, for example (V) and (VIII), in contrast to primary arylamides, form halochromic salts with 85% formic acid. This fact indicates that it is possible to use certain organic acids for the synthesis of heterocyclic compounds based on the arylamides of hydroxycarboxylic acids.



(I) R = CH_3, (II) R = C_2H_5, (III) R = n-C_4H_9

(IV) R = CH_3, R′ = p-$CH_3C_6H_4$; (V) R = CH_3, R′ = p-$CH_3OC_6H_4$; (VI) R = C_2H_5, R′ = C_6H_5; (VII) R = C_2H_5, R′ = p-$CH_3C_6H_4$; (VIII) R = C_2H_5, R′ = p-$CH_3OC_6H_4$; (IX) R = n-C_4H_9, R′ = C_6H_5

(X) R = CH_3, R′ = p-$CH_3C_6H_4$; (XI) R = CH_3, R′ = p-$CH_3OC_6H_4$; (XII) R = C_2H_5, R′ = C_6H_5; (XIII) R = C_2H_5, R′ = p-$CH_3C_6H_4$; (XIV) R = C_2H_5, R′ = p-$CH_3OC_6H_4$; (XV) R = n-C_4H_9, R′ = C_6H_5

EXPERIMENTAL

Ethyl N-Methyloxanilate (I). To a solution of 16 g of N-methylaniline in 30 ml of dry pyridine was added in small portions, with stirring and cooling, 22.9 g of ethoxalyl chloride. The flask contents were poured into 150 ml of water, and the reaction product was extracted with ether and dried over calcium chloride. After removing the solvent the residue was vacuum-distilled. Yield 16 g (51.7%).

B. p. 157-159° (5 mm), n_D^{20} 1.5160, d_{20}^{20} 1.1275, MR_D 55.33; calc. 55.00. Found %: N 6.53, 6.65. $C_{11}H_{13}O_3N$. Calculated %: N 6.76.

Ethyl N-Ethyloxanilate (II). To a solution of 30.25 g of N-ethylaniline in 50 ml of ether, with cooling and stirring, was added a solution of 17 g of ethoxalyl chloride in 30 ml of ether. After heating on the water bath for 10-15 minutes the mixture was treated with 50 ml of water, and further treatment was the same as in the preceding experiment. Yield 20 g (74%). B.p. 168-169.5° (10 mm). From [3]: b.p. 215-220°.

Ethyl N-(n-Butyl)-oxanilate (III). For the reaction we took 29.8 g of N-butylaniline in 50 ml of ether and 13.6 g of ethoxalyl chloride in 15 ml of ether. Yield 18 g (72%);

B.p. 188-189° (10 mm), d_{18}^{18} 1.0708, n_D^{18} 1.5050, MR_D 69.06; calc. 68.86. Found %: N 5.45, 5.57. $C_{14}H_{19}O_3N$. Calculated %: N 5.62.

N-Methylanilide of p-Tolilic Acid (IV). Obtained by the reaction of 6.2 g of (I) with the p-tolylmagnesium bromide prepared from 10.5 g of p-bromotoluene and 15 g of magnesium in 40 ml of ether. The organomagnesium complex was decomposed with saturated ammonium chloride solution. Readily soluble in alcohol, ether, acetic acid and benzene, and difficultly soluble in benzine. With concentrated sulfuric acid it forms a transient red color. Yield 3.5 g (33.8%). Needles (from benzine) with m.p. 74-75°.

Found %: N 4.00, 4.31. $C_{23}H_{23}O_2N$. Calculated %: N 4.05.

N-Methylanilide of 4, 4'-Dimethoxybenzilic Acid (V). Starting substances: 6.2 g of (I), 14.5 g of p-iodoanisole and 1.5 g of magnesium. Readily soluble in alcohol, acetic acid and benzene, and difficultly soluble in ether and benzine. Dissolves in concentrated sulfuric acid or 85% formic acid with the formation of a vanishing red-violet color. Yield 4.5 g (40%). Needles, collecting in clusters (from methanol). M.p. 126-126.5°.

Found %: N 3.59, 3.86. $C_{23}H_{23}O_4N$. Calculated %: N 3.70.

N-Ethylanilide of Benzilic Acid (VI). For reaction we took 6.6 g of (II), 14.04 g of bromobenzene and 2.2 g of magnesium. Soluble in benzene, alcohol and acetic acid. With concentrated sulfuric acid it gives a vanishing brown color. Yield 8.8 g (88.6%). Needles (from alcohol) with m.p. 98.5°. From [1]: m.p. 97.5-98.5°.

N-Ethylanilide of p-Tolilic Acid (VII). Starting substances 6.6 g of (II), 15.4 g of p-bromotoluene and 2.2 g of magnesium. Readily soluble in acetic acid, benzere and ether, and difficultly soluble in alcohol and benzine. With concentrated sulfuric acid it gives a vanishing crimson color. Yield 8.3 g (77.1%). Rods (from alcohol) with m.p. 111-112°.

Found %: N 3.60, 3.66. $C_{24}H_{25}O_2N$. Calculated %: N 3.89.

N-Ethylanilide of 4, 4'-Dimethoxybenzilic Acid (VIII). Reaction was between 6.6 g of (II) and the p-anisylmagnesium iodide obtained from 21.1 g of p-iodoanisole and 2.2 g of magnesium. Readily soluble in benzene, ether and acetic acid, and difficultly soluble in alcohol and benzine. With concentrated sulfuric acid, and also with 85% formic acid, it forms a vanishing red-violet color. Yield 9.2 g (78.4%). Long needles (from alcohol) with m.p. 97.5°.

Found %: N 3.69, 3.75. $C_{24}H_{25}O_4N$. Calculated %: N 3.58.

N-Butylanilide of Benzilic Acid (IX). Starting substances: 7.47 g of (III), 18.8 g of bromobenzene and 2.9 g of magnesium. Difficultly soluble in benzine and readily soluble in other organic solvents. With concentrated sulfuric acid it gives a rapidly vanishing red color. Yield 7.1 g (65.7%). Plates (from alcohol) with m.p. 80.5-81.5°.

Found %: N 3.85, 3.97. $C_{24}H_{25}O_2N$. Calculated %: N 3.92.

1-Methyl-3,3-di-(p-tolyl)-oxindole (X). A solution of 1 g of (IV) in 10 ml of glacial acetic acid was treated with 1 ml of concentrated sulfuric acid. On conclusion of reaction (disappearance of the red-brown color) the flask contents were poured into 30 ml of water, and the precipitate obtained here was worked up in known manner. Yield 0.5 g (51%). Plates (from alcohol) with m.p. 120-120.5°.

Found %: N 4.43, 4.35. $C_{23}H_{21}ON$. Calculated %: N 4.26.

1-Methyl-3,3-di(p-anisyl)-oxindole (XI). For reaction we took: 1 g of (V) in 10 ml of glacial acetic acid and 1 ml of concentrated sulfuric acid. Yield 0.5 g (52.5%). Needles (from alcohol) with m.p. 146.5-148°.

Found %: N 4.07. $C_{23}H_{21}O_3N$. Calculated %: N 3.90.

1-Ethyl-3,3-diphenyloxindole (XII). Starting substances: 2 g of (VI) in 10 ml of glacial acetic acid and 4 ml of concentrated sulfuric acid. Yield 1.74 g (92%). Hexagonal prisms (from alcohol) with m.p. 158-159°. From [1]: m.p. 158-159°.

1-Ethyl-3,3-di-(p-tolyl)-oxindole (XIII). Obtained from 2 g of (VII) in 10 ml of glacial acetic acid and 2 ml of concentrated sulfuric acid. Readily soluble in benzene, ether and acetic acid, and difficultly soluble in alcohol and benzine. Yield 1.72 g (85.3%). Prisms (from alcohol) with m.p. 119.5°.

Found %: N 3.95, 4.15. $C_{24}H_{23}ON$. Calculated %: N 4.10.

1-Ethyl-3,3-di-(p-anisyl)-oxindole (XIV). For reaction we took 1 g of (VIII) in 5 ml of glacial acetic acid and 1 ml of concentrated sulfuric acid. Readily soluble in acetic acid, benzene and ether, and difficultly soluble in alcohol and benzine. Yield 0.74 g (77.6%). Plates (from alcohol) with m.p. 104-106°.

Found %: N 3.94, 3.96. $C_{24}H_{23}O_3N$. Calculated %: N 3.75.

1-Butyl-3,3-diphenyloxindole (XV) was obtained in 89% yield by the treatment of an acetic acid solution of (IX) with concentrated sulfuric acid. Readily soluble in acetic acid, benzene and toluene, and difficultly soluble in alcohol and benzine. Prisms (from alcohol) with m.p. 110-112°.

Found %: N 4.03, 4.10. $C_{24}H_{23}ON$. Calculated %: N 4.13.

SUMMARY

1. A method was developed for the preparation of N-alkylated arylamides of α-hydroxycarboxylic acid; in this connection a number of previously unknown compounds were synthesized and their properties studied.

2. The reaction of ethoxalyl chloride with n-butylaniline gave the previously unknown n-butyloxanilic acid ester, and its properties were studied.

3. It was shown that when treated with concentrated sulfuric acid the N-alkylarylamides of α-hydroxycarboxylic acids are converted in high yields into the N-alkyl derivatives of 3,3-diaryloxindoles; here a number of compounds were obtained for the first time and their properties were studied.

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CHEMISTRY OF HETEROCYCLES

XXX. 2,4-DIHALO DERIVATIVES OF 9-PHENYLACRIDINE

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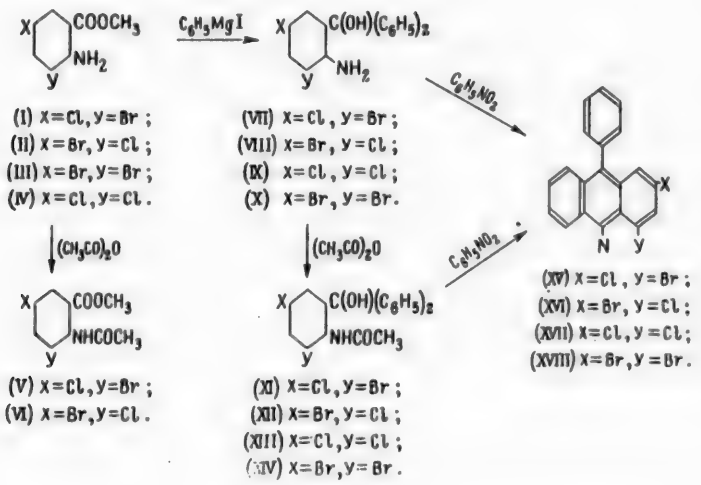
As a continuation of previous work [1], we synthesized the 2,4-dihalo derivatives of 9-phenylacridine, in accord with the following scheme



The methyl esters of the 3, 5-dihaloanthranilic acids (I, II, III) were obtained by the halogenation of the methyl esters of 5-chloro- and 5-bromoanthranilic acids. To synthesize the bromo derivatives (I, III) we first attempted to use N-chloroacetamide. However, the experiments revealed that the latter gives good results only in the preparation of mono-, but not of dibromo derivatives. Since (I) and (II) have the same melting points, then to characterize them we prepared the N-acetyl derivatives (V) and (VI). The reaction of I-IV with phenylmagnesium iodide yields the 3,5-dihalo-2-aminotriphenylcarbinol derivatives (VII-X). The latter are insoluble in dilute mineral acids and concentrated hydrochloric acid. They form colored solutions with concentrated sulfuric acid, which is explained by the appearance of halochromism. When these solutions are diluted with water the dihalo derivatives of the 2-aminotriphenylcarbinol are reprecipitated. With acetic anhydride they readily give the N-acetyl derivatives (XI-XIV), which are also characterized by halochromism.

The dihalo derivatives of 2-aminotriphenylcarbinol (VII-X), and also their N-acetyl derivatives (XI-XIV), when heated in nitrobenzene are converted into the 2,4-dihalo derivatives of 9-phenylacridine. In this connection the dihalo derivatives of 2-aminotriphenylcarbinol show easier cyclization to give the acridine ring than do their N-acetyl derivatives. Thus, the reaction with the N-acetyl derivatives requires 4 hours, whereas the corresponding carbinols are converted into the free acridine bases in a matter of 30 minutes. In contrast to the 4-halo derivatives [1], the 2, 4-dihalo derivatives of 9-phenylacridine (XV-XVIII) are insoluble in dilute mineral acids and do not give picrates with picric acid. They are soluble only in concentrated acids with the formation of a yellow-green fluorescence.

EXPERIMENTAL

Methyl 3-Bromo-5-chloroanthranilate (I). To a solution of 1.85 g of methyl 5-chloroanthranilate in 10 ml of 80% acetic acid was added 0.5 ml of concentrated sulfuric acid and a solution of 1.03 g of sodium bromide in a small amount of water. For bromination we used 0.64 g of N, N-dichlorourea (temperature not above 25-30°). On conclusion of reaction (test with starch-iodide paper) the reaction mixture was poured into 50 ml of water and the obtained precipitate was worked up in the usual manner. Readily soluble in ether, alcohol, benzene and acetic acid. Yield 1.7 g (64.4%). Slender needles (from methanol) with m.p. 76-76.5°.

Found %: N 5.45, 5.62. $C_8H_7O_2NBrCl$. Calculated %: N 5.29.

Methyl N-Acetyl-3-bromo-5-chloroanthranilate (V). A solution of 1.5 g of (I) in 5 ml of acetic anhydride was heated in a sand bath for 1.5 hours and then poured into 20 ml of water. The precipitate obtained was filtered and recrystallized from alcohol. Soluble in alcohol, acetic acid and acetone. Yield 1.55 g (89%). Hexagonal prisms with m.p. 117-119°.

Found %: N 4.43, 4.56. $C_{10}H_9O_3NBrCl$. Calculated %: N 4.57.

Methyl 3-Chloro-5-bromoanthranilate (II). For reaction we took 4.6 g of methyl 5-bromoanthranilate in 15 ml of 80% acetic acid, 0.5 ml of concentrated sulfuric acid and 1.29 g of N, N-dichlorourea. Soluble in alcohol, ether, benzene and acetic acid. Yield 2.6 g (49.2%). Needles (from methanol) with m.p. 76-76.5°.

Found %: N 5.35, 5.45. $C_8H_7O_2NBrCl$. Calculated %: N 5.29.

Methyl N-Acetyl-3-chloro-5-bromoanthranilate (VI). Soluble in alcohol, acetic acid and acetone. Hexagonal prisms (from alcohol) with m.p. 120.5-123°.

Found %: N 4.52, 4.50. $C_{10}H_9O_3NBrCl$. Calculated %: N 4.57.

Methyl 3, 5-Dibromoanthranilate (III). Starting substances: a solution of 13.8 g of methyl 5-bromoanthranilate in 50 ml of 80% acetic acid, a solution of 6.18 g of sodium bromide in a small amount of water, 3 ml of concentrated sulfuric acid and 3.9 g of dichlorourea. Yield 16.2 g (88.8%). Needles (from methyl alcohol) with m.p. 85.5-87°. From [2]: m.p. 84, 90°.

3-Bromo-5-chloro-2-aminotriphenylcarbinol (VII). Obtained by the reaction of 13.22 g of (I) and 0.2 mole of phenylmagnesium iodide. Readily soluble in alcohol, benzine, acetone and glacial acetic acid. Gives a red color with concentrated sulfuric acid. Yield 12.5 g (64.4%). Plates (from benzine) with m.p. 113-114.5°.

Found %: N 3.72, 3.67; Cl + Br 29.72, 29.69. $C_{19}H_{15}ONBrCl$. Calculated %; N 3.69; Cl + Br 29.70.

N-Acetyl-3-bromo-5-chloro-2-aminotriphenylcarbinol (XI). For reaction we took 4 g of (VII) and 10 ml of acetic anhydride. Time of heating was 1 hour. Readily soluble in benzene and toluene, and difficultly soluble in alcohol and acetic acid. Gives a dark-red color with concentrated sulfuric acid. Yield 3 g (67.7%). Prisms (from glacial acetic acid) with m.p. 190-192°.

Found %: N 3.05, 3.08. $C_{21}H_{17}O_2NBrCl$. Calculated %: N 3.25.

3-Chloro-5-bromo-2-aminotriphenylcarbinol (VIII). Starting substances: 10.58 g of (II) and 0.16 g of phenylmagnesium iodide. Soluble in alcohol, acetic acid, benzine and acetone. Dissolves in concentrated sulfuric acid with the formation of a red color. Yield 10.3 g (66.3%). Needles (from benzine) with m.p. 116-118°.

Found %: N 3.52, 3.56; Br + Cl 29.45, 29.40. $C_{19}H_{15}ONBrCl$. Calculated %: N 3.69; Br + Cl 29.70.

N-Acetyl-3-chloro-5-bromo-2-aminotriphenylcarbinol (XII). Soluble in alcohol, acetic acid and benzene. Gives a dark-red color with concentrated sulfuric acid. Prisms (from glacial acetic acid) with m.p. 192-193°.

Found %: N 3.16, 2.96. $C_{21}H_{17}O_2NBrCl$. Calculated %: N 3.25.

3-5-Dichloro-2-aminotriphenylcarbinol (IX). For reaction we took 11 g of methyl 3, 5-dichloroanthranilate (IV),* 40 g of iodobenzene and 4.8 g of magnesium. Soluble in alcohol, benzine, ether, benzene and acetic acid. Gives a dark-red color with concentrated sulfuric acid. Yield 10.6 g (61.6%). Needles (from alcohol) with m.p. 112.5-113.5°.

* Obtained by the esterification of 3, 5-dichloroanthranilic acid. M.p. 63-64°. From [3]: m.p. 63-64°.

Found %: N 4.11, 3.84; Cl 20.54, 20.31. $C_{19}H_{15}ONCl_2$. Calculated %: N 4.07: Cl 20.62.

N-Acetyl-3, 5-dichloro-2-aminotriphenylcarbinol (XIII). Soluble in benzene, ether, acetic acid and alcohol. Needles (from glacial acetic acid) with m.p. 179-180°.

Found %: N 3.73, 3.73. $C_{21}H_{17}O_2NCl_2$. Calculated %: N 3.62.

3, 5-Dibromo-2-aminotriphenylcarbinol (X). For reaction we took 14.8 g of (III) and 0.192 mole of phenylmagnesium iodide. Soluble in alcohol, benzine, benzene, acetone and acetic acid. Its solutions in concentrated sulfuric acid are colored a dark-red. Yield 13.5 g (64.96%). Needles (from benzine) with m.p. 112-113°.

Found %: N 3.07, 3.09; Br 36.62, 36.76. $C_{19}H_{15}ONBr_2$. Calculated %: N 3.23; Br 36.93.

N-Acetyl-3, 5-dibromo-2-aminotriphenylcarbinol (XIV). Soluble in alcohol, acetic acid and benzene. Gives a dark-red color with concentrated sulfuric acid. Rods (from glacial acetic acid) with m.p. 206-207°.

Found %: N 2.69, 2.64. $C_{21}H_{17}O_2NBr_2$. Calculated %: N 2.94.

2-Chloro-4-bromo-9-phenylacridine (XV). a) A solution of 4 g of (VII) in 4 ml of nitrobenzene was heated for 30 minutes. The precipitate obtained on cooling was filtered, washed with alcohol, and air-dried. Yield 3 g (79%).

b) A mixture of 1.5 g of (XI) and 2 ml of nitrobenzene was boiled for 4 hours on a sand bath. The nitrobenzene was steam-distilled, and the reaction product was extracted from the tarry residue with concentrated hydrochloric acid. The free acridine base was precipitated by the addition of ammonia to the hydrochloric acid extract. Yield 0.79 g (61.5%). Readily soluble in benzene, and difficultly soluble in acetic acid and alcohol. Dissolves in concentrated sulfuric acid with a yellow-green fluorescence. Yellow needles (from benzene) with m.p. 228-229°.

Found %: Cl+Br 31.44, 31.14; N 3.78, 3.87. $C_{19}H_{11}NBrCl$. Calculated %: Cl+Br 31.31; N 3.80.

2-Bromo-4-chloro-9-phenylacridine (XVI). Obtained, as described above, from 4 g of (VIII) in 4 ml of nitrobenzene (yield 2.1 g, 55.4%), or from 1.5 g of (XII) in 2 ml of nitrobenzene (yield 0.85 g, 66.2%). Readily soluble in benzene and toluene, and difficultly soluble in acetic acid and alcohol. Dissolves in concentrated sulfuric and hydrochloric acid with the formation of a yellow-green fluorescence. Light-yellow needles (from benzene) with m.p. 214-215°.

Found %: N 3.86, 3.96; Cl+Br 31.20, 31.15. $C_{19}H_{11}NBrCl$. Calculated %: N 3.80; Cl+Br 31.31.

2, 4-Dichloro-9-phenylacridine (XVII). Obtained from 2 g of (IX) in 2 ml of nitrobenzene (yield 1.15 g, 61.1%), or from 1 g of (XIII) in 1 ml of nitrobenzene (yield 0.45 g, 53.6%). Difficultly soluble in alcohol and ether, and readily soluble in benzene and acetic acid. Its solutions in concentrated mineral acids show a weak yellow-green fluorescence. Light-yellow needles (from glacial acetic acid) with m.p. 213-213.5°.

Found %: N 4.32, 4.21; Cl 21.55, 21.89. $C_{19}H_{11}NCl_2$. Calculated %: N 4.33; Cl 21.89.

2, 4-Dibromo-9-phenylacridine (XVIII). Obtained from 4 g of (X) in 4 ml of nitrobenzene (yield 2.55 g, 66.8%), or from 1 g of (XIV) in 1 ml of nitrobenzene (yield 0.55 g, 63.3%). Difficultly soluble in alcohol, acetone and acetic acid, and readily soluble in benzene, toluene and chloroform. With concentrated hydrochloric and sulfuric acids it gives solutions with a yellow-green fluorescence. Light-yellow needles (from benzene) with m.p. 232-233°.

Found %: N 3.69, 3.45; Br 38.72, 38.94. $C_{19}H_{11}NBr_2$. Calculated %: N 3.39; Br 38.72.

SUMMARY

1. Based on the 3, 5-dihalo derivatives of 2-aminotriphenylcarbinol and their N-acetyl derivatives we developed a method for the preparation of the 2, 4-dihalo derivatives of 9-phenylacridine.

2. It was established that the dihalo derivatives of 2-aminotriphenylcarbinol show much easier cyclization to the acridine ring than do their N-acetyl derivatives.

3. We used N, N-dichlorourea to obtain the methyl esters of 3, 5-dihaloanthranilic acids in good yields;

here we obtained a number of previously unknown compounds and studied their properties.

4. The reaction of phenylmagnesium halide with the methyl esters of 3, 5-dihaloanthranilic acids gave some new dihalo derivatives of 2-aminotriphenylcarbinol, and also their N-acetyl derivatives. The properties of these compounds were studied.

5. Some previously unknown 2, 4-dihalo derivatives of 9-phenylacridine were prepared and their properties were studied.

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** In Russian.

THE MICROSTRUCTURE OF PROTEIN

XIV. THE PIPERAZIDES OF AMINO ACIDS

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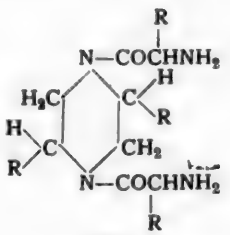
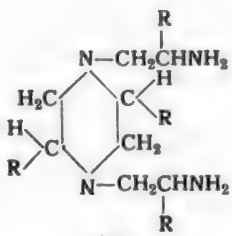
At first derivatives of piperazine with amino acids were isolated from proteins in their reduction [1]. The reduction experiments served as evidence of the preformation of cyclic anhydrides in protein molecules, capable of being converted into piperazines on reduction [2-3]. These investigations served as a start for the synthesis of piperazine-amino acid derivatives. In 1925-1926 methods for the synthesis of such derivatives were developed [4]. As a result, the following compounds of piperazines with amino acids and peptides were obtained: N, N'-dialanyl-, N,N'-dileucyl-, N,N'-di(glycyl-leucyl)- and N,N'-di(alanyl-leucyl)-piperazides and N,N'-diglycyl-, N,N'dileucyl-, N,N'-di-(glycyl-leucyl)-, N,N'-di-(alanyl-leucyl)- and N,N'-di-(alanyl-leucyl)-dimethylpiperazides. The Fischer method, proposed by him for the preparation of peptides, was chosen for the synthesis of the enumerated compounds. The method was reduced to the acylation of piperazine with either the chlorides or bromides of α-haloaliphatic acids [5] and subsequent replacement of the halogen atom by the amino group using ammonia.

Recently a new method was proposed for the preparation of such piperazine derivatives. It consisted in the reaction of amino acid azides with piperazine [6]. The synthesis methods that have been developed permit obtaining amino acid piperazides with the general formula (I). The reduction of proteins with strong reducing agents leads only to substituted piperazines (II).



(I)



(II)

As a result, the substituted piperazines, isolated from proteins in the reduction of the latter with sodium in alcohols and with aluminum lithium hydride [3], will differ in their properties from synthetic piperazides. A study of the properties of the latter compounds is of great interest in the light of contemporary theories on the structure of the protein molecule, according to which both piperazines and tripeptides participate in the building of the micromolecular structure. At the present time we have a number of methods available for the analysis of the protein structure, which have justified themselves both in establishing the lengths of the peptide chains in a protein molecule [7] and in quantitatively giving the number of rings contained in them [8]. We refer to the use of spectrophotometric studies of the copper complexes of proteins and the electrolytic reduction of proteins.

In the present investigation we proposed to study the piperazides of some amino acids and peptides using the above mentioned methods. For this we synthesized a dipeptide piperazide and a tripeptide piperazide, both previously unknown, by the Abderhalden procedure. The formation of the copper complexes was studied. The results of studying the copper complexes of the di- and tripeptide piperazides revealed (Table) that they are somewhat different from those of the di- and tripeptides themselves. This difference is especially noticeable for

the tripeptide piperazide. As is known, the absorption maximum of the copper complex of the linear tripeptide is found at a wavelength of 575 mμ [9]. The absorption maximum of the tripeptide piperazide is shifted toward shorter wavelengths and is found at 530 mμ. This shift of the maximum for the tripeptide piperazide when compared with the tripeptide is without doubt due to the presence of the piperazine ring, functioning as an amide group in the tripeptide. The ability of the tripeptide piperazide to form a complex of the tetrapeptide type will permit us to confirm the presence of an N-aminoacyl type of bond in electroreduced protein also by the absorption spectrum of its copper complex.

TABLE

Optical Density Values of Copper Complexes of Di- and Tripeptide Piperazides

λ in mμ	ε_1 of dipeptide piperazide	ε_2 of tripeptide piperazide	λ in mμ	ε_1 of dipeptide piperazide	ε_2 of tripeptide piperazide
500	0.163	0.401	570	0.419	0.370
510	0.191	0.422	580	0.460	0.358
520	0.216	0.429	590	0.489	0.344
530	0.251	**0.439**	600	0.505	0.324
540	0.291	0.421	**610**	**0.517**	0.308
550	0.334	0.407	620	0.505	0.291
560	0.376	0.397	630	0.488	0.276

EXPERIMENTAL

Di(bromoisocaproyl)piperazine was prepared by the method of [7]. M.p. 141-142°, from the literature: m.p. 142°. Yield 65%.

Preparation of Dileucylpiperazine (Hydrobromide). A mixture of 22 g of the bromoisocaproylpiperazine and alcoholic ammonia (261 g of NH_3 in 2.100 liters of CH_3OH, i.e., 150 moles) was allowed to stand at room temperature for 3 days. After concentration in vacuo, the oily residue in the flask was treated with anhydrous alcohol until a precipitate was obtained, which was then filtered and washed on the filter with alcohol. The substance, dried in a vacuum-desiccator over H_2SO_4, had m.p. 300° (with decompn.). Weight 7.5 g. Gives neither the biuret nor the anhydride reaction. The ninhydrin reaction was negative. When heated in water with quinone it gives a red color, and on cooling a red precipitate deposits.

Found %: N 11.77; NH_2 5.35 (formalin). $C_{16}H_{34}O_2N_4Br_2$. Calculated %: N 11.81; NH_2 5.91.

Preparation of Bromobutyryl-leucylpiperazine. Six grams of the dileucylpiperazine salt was dissolved in 100 ml of water, and with mechanical stirring and cooling, to the solution was added in portions 9.5 g of α-bromobutyryl bromide and 8.2 g of $NaHCO_3$ (anhydrous). On conclusion of reaction (disappearance of acid bromide odor) the solution was extracted with chloroform. The chloroform solution, dried over Na_2SO_4 and filtered, was concentrated in vacuo to an oily residue. After adding anhydrous alcohol the solution was again concentrated in vacuo to remove traces of chloroform. The precipitate obtained here was filtered and washed with alcohol. Weight of the dry precipitate 3.2 g. M.p. 187-189°. Not reported in the literature. Does not give the ninhydrin reaction; the reaction with quinone is negative.

Found %: C 47.13; H 7.09; N 9.17. $C_{24}H_{42}O_4N_4Br_2$. Calculated %: C 47.20; H 6.94; N 9.18.

Preparation of Aminobutyryl-leucylpiperazine. A mixture of 3.2 g of the bromobutyryl-leucylpiperazine and alcoholic ammonia (23.6 g of NH_3 in 200 ml of anhydrous C_2H_5OH, i.e., 120 moles) was allowed to stand at room temperature for 7 days. The precipitate, obtained in the standing of this solution, was filtered. The filtrate was precipitated with absolute ether. Weight of obtained precipitate 1.5 g. M.p. 287-290°. Not reported in the literature. Does not give the ninhydrin reaction. The biuret reaction is positive. Its absorption maximum lies at 610 mμ. The reaction with Nessler reagent is negative, while with quinone it gives a red color.

Found %: C 44.44; H 7.46; N 13.38; NH_2 3.89 (formalin) NH_2 4.24 (Willstätter). $C_{24}H_{48}O_4N_6Br_2$. Calculated %: C 44.72; H 7.51; N 13.04; NH_2 4.34.

Preparation of Bromobutyryl-aminobutyryl-leucylpiperazine. The coupling was run in the same manner as described for the bromobutyryl-leucylpiperazine.

Preparation of Aminobutyryl-aminobutyryl-leucylpiperazine. Liquid ammonia was used for the amination (in a sealed ampoule for 7 days). The isolated substance was purified by recrystallization from alcohol. Yield 0.2 g, from 0.6 g of bromo derivative taken for reaction. M.p. 320° (with decompn.). Not reported in the literature. Does not give the ninhydrin reaction. The reaction with Nessler reagent is negative, while with quinone it gives a red color. The biuret reaction is positive. Its absorption maximum lies at 530 mμ.

Found %: C 46.99, 47.06; H 7.84, 7.88; N 14.17, 14.20. $C_{22}H_{42}O_6N_8Br_2$. Calculated %: C 47.17; H 7.67; N 13.76.

SUMMARY

1. We synthesized the di- and tripeptide piperazides: N,N'-aminobutyryl-leucyl and N,N'-aminobutyryl-aminobutyryl-leucyl piperazides.

2. It was shown that the absorption maximum of the tripeptide piperazide copper complex lies at a wavelength of 530 mμ.

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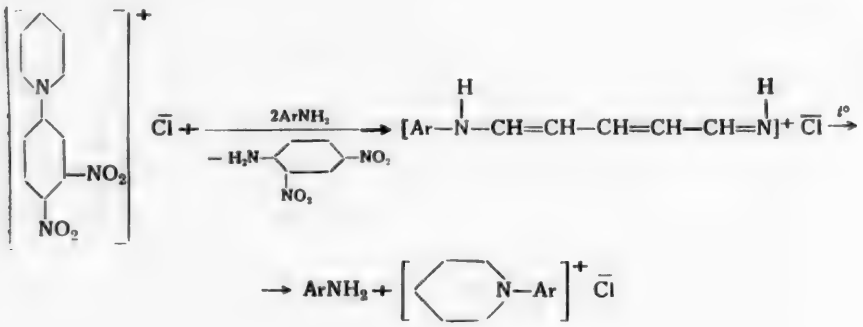
CATALYTIC HYDROGENATION OF N-ARYL SUBSTITUTED PYRIDINE SALTS

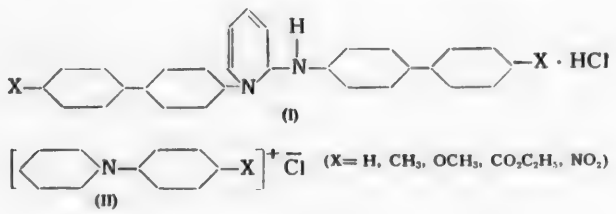
N. E. Grigoryeva, A. B. Oganesyan and I. A. Mysh

A widely known method for the preparation of piperidine derivatives is the catalytic hydrogenation of pyridine systems [1, 2]. However, the difficult availability of pyridine compounds limits the utility of this method. This also applied fully to the preparation of N-arylpiperidines by this method. The known method of obtaining N-aryl derivatives of piperidine by the condensation of 1, 5-dibromopentane with salts of aromatic amines [3] was only of historical interest until recently, due to the difficult availability of 1, 5-dibromopentane. It is known that pyridine salts are hydrogenated more easily than are the pyridines themselves [4, 5]; in turn, the alkyl halide salts are hydrogenated more easily than are the hydrogen halide salts of the pyridine, and it could be expected that replacement of the alkyl by aryl, possessing electron-acceptor properties, will favor loosening of the pyridine ring electron system and facilitate the addition of hydrogen.

We prepared the pyridine hydrochlorides by the cyclization of the dianil hydrochlorides of glutaconic dialdehyde (pyridine dyes) [6] without isolation of the latter, by the scheme



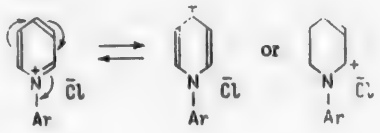
A systematic study of this reaction revealed that the cyclization of the dye is not always accompanied by cleavage of the amine molecule, as it is shown in the scheme. Thus, the cyclization of biphenyl derivatives [7] yields compounds having the same composition as the starting dyes; the theory was expressed that they represent the hydrochlorides of the N, α-substituted derivatives of the dihydropyridine:



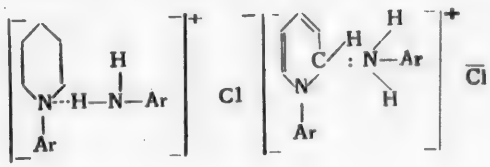
(I)

(II) (X= H, CH_3, OCH_3, $CO_2C_2H_5$, NO_2)

Compounds (I) show different stability to hydrolysis depending on the character of substituent X and the stability decreases in the order: $NH_2 > H > NO_2$. Compound (I) ($X = NH_2$) is hydrogenated very easily, which, it would seem, supports the presence of a dihydropyridine ring in it. Later, when the pyridine chlorobiphenylate [8] was obtained from this compound, it proved to also hydrogenate easily. The hydrogenation of other N-substituted pyridine chlorophenylate salts and four of its p-derivatives is also easily accomplished. We did not study the hydrogenation kinetics of these salts and cannot present quantitative data on the hydrogenation rate of various substituted pyridine chlorophenylate derivatives, but the fact that they hydrogenate in the same manner as unsaturated compounds, for example cinnamic acid, is evidence that these salts are not quaternary pyridine salts with an electron system, responsible for the inertness of the pyridine ring. It is quite probable that the N-aryl substituted pyridine salts represent carbonium salts or a mixture of the two types of salts shown below



and depending on the electron-acceptor strength of the aromatic radical the equilibrium can shift toward one of them. As a result, it was qualitatively shown that the pyridine ring in all of the examined N-aryl substituted salts has a weakened electron system and depending on the basicity of the amines, cleaved in the cyclization of the pyridine dyes (see scheme), they can form more or less stable addition products with the pyridine salt, either through the hydrogen bond between the nitrogens [9] or through the pair of electrons between the nitrogen of the amino group and the unsaturated carbon atom.



The hydrogenations were run at room temperature with Pt-catalyst (PtO_2) in methyl alcohol solution. In all cases, except one, only the pyridine ring was hydrogenated; in the case of pyridine p-nitrochlorophenylate, besides the pyridine ring, the nitro group was also reduced, so this method cannot be used to obtain the hydrochloride of N-(p-nitrophenyl)-piperidine. The hydrogenation products were studied as the N-arylpiperidine hydrochlorides and picrates. The properties of N-arylpiperidine hydrochlorides have never been studied. When freshly prepared they are colorless crystalline compounds, but on storage they assume yellow, pink or lilac hues. The N-arylpiperidine hydrohalides are capable of various types of condensations with the formation of colored compounds, a study of which is the subject of our investigations at the present time. The preparation of N-arylpiperidine hydrohalides by the hydrogenation of the corresponding pyridine salts can have preparative value, since the latter are readily available compounds.

EXPERIMENTAL

Pyridine Chloroarylates. The method of preparing pyridine chloroarylates by the cyclization of pyridine dyes without the isolation of the latter [6] was modified somewhat, which permitted a reduction in the time required to prepare these salts. The mixture of starting substances– pyridine 2, 4-dinitrochlorophenylate and amine in alcohol–was heated until the pyridine 2, 4-dinitrochlorophenylate had decomposed completely (absence of a violet color when the alcohol solution was mixed with alkali). Then the alcohol was removed by distillation, while the mixture of dye and dinitroaniline was heated with water until all of the dye had decomposed. The precipitate of dinitroaniline and secondary amine (if crystalline) was filtered and washed with water. The filtrate was extracted with either benzene or ether to remove amine traces, decolorized with carbon, and evaporated to dryness. The salts were purified by recrystallization from anhydrous alcohol or by precipitation from alcohol with ether.

Hydrogenation. Platinum dioxide was prepared by the fusion of chloroplatinic acid • with sodium nitrate [11]. The hydrogenation was run in an apparatus, consisting of a pear-shaped flask, measuring cylinder and pressure cylinder [12]. The hydrogen, obtained by the treatment of arsenic-free zinc with sulfuric acid, was purified by passage through concentrated potassium permanganate solution, concentrated sulfuric acid, and dry potassium hydroxide. The solvent—methyl alcohol—was treated with sulfuric acid, then with alkali, and distilled through an efficient column, b.p. 65°. For synthetic methyl alcohol (without foreign odor) its distillation through a column is sufficient. Microanalysis methods were used to determine the nitrogen and chlorine in the hydrogenation products and their derivatives.

1. N-Phenylpiperidine Hydrochloride. A solution of 2 g of pyridine chlorophenylate in 70 ml methyl alcohol was poured into the hydrogenation bulb, and then 100 mg of catalyst (PtO_2) was added. The hydrogen absorbed was 770 ml (including the hydrogen consumed for the reduction of the platinum oxide), which is approximately 3 moles. The catalyst was filtered through a Schott crucible and washed several times with methyl alcohol. During washing the catalyst flashed occasionally, which was evidence that the catalyst was still active after hydrogenation. During filtration the colorless solution of the salt turned yellow. Removal of the alcohol by distillation gave a crystalline product with a slight yellow color (1.9 g); recrystallization from an alcohol-ether mixture (with carbon) gave colorless crystals (1.31 g), m.p. 202°.

Found %: N 7.08, 7.10; Cl 18.03, 18.03. $C_{11}H_{16}NCl$. Calculated %: N 7.11; Cl 17.97.

N-Phenylpiperidine Picrate, recrystallized twice from water, had m.p. 129-130°.

Found %: N 15.13, 15.20. $C_{17}H_{18}O_7N_4$. Calculated %: N 14.97.

2. N-(p-Methylphenyl)-piperidine Hydrochloride. A mixture of 5.3 g of pyridine p-methylchlorophenylate and 150 mg of catalyst in 50 ml of methyl alcohol was hydrogenated for 2 hours and 20 minutes. The amount of hydrogen absorbed was 1960 ml (3 moles). The residue (5.5 g) after distilling off the alcohol was decolorized with carbon and precipitated twice from anhydrous alcohol with ether. Colorless silky crystals (3.29 g), m.p. 200-201°. On storage the salt rapidly turned yellow and volatilized.

Found %: N 7.14, 7.09. $C_{12}H_{18}NCl$. Calculated %: N 6.62.

N-(p-Methylphenyl)-piperidine Picrate was recrystallized from aqueous alcohol, m.p. 171°.

Found %: N 13.97. $C_{18}H_{20}O_7N_4$. Calculated %: N 13.90.

3. N-(p-Methoxyphenyl)-piperidine Hydrochloride. A mixture of 3.4 g of pyridine p-methoxychlorophenylate and 108 mg of catalyst in 50 ml of methyl alcohol was hydrogenated for 2.5 hours, at the end of which time 1030 ml (3 moles) of hydrogen had been absorbed. After removing the catalyst by filtration the solution became very dark. The alcohol was removed completely by distillation, and the residue was dried in a vacuum-desiccator. After decolorization with carbon and two precipitations from anhydrous alcohol with ether the salt was obtained as silky, slightly grayish crystals (2.9 g), m.p. 186-187°.

Picrate, recrystallized from water, had m.p. 176-177°.

Found %: N 13.34, 13.36. $C_{18}H_{20}O_8N_4$. Calculated %: N 13.30.

4. N-(p-Carbethoxyphenyl)-piperidine Hydrochloride. A mixture of 3 g of pyridine p-carbethoxychlorophenylate and 113 mg of catalyst in 50 ml of alcohol was hydrogenated for 2 hours and 55 minutes, at the end of which time 820 ml (3 moles) of hydrogen had been absorbed. Removal of the solvent by distillation, and then by evaporation, gave 2.07 g of the dry salt as a finely crystalline yellow powder. This salt is more volatile than the other piperidine salts, and perceptible losses are obtained even with very slow fractional distillation of the solvent. The losses decrease if a part of the alcohol is distilled off, and then the salt precipitated by the addition of ether, but here a large excess of ether is needed. After recrystallization from an alcohol-ether mixture the salt was obtained as colorless crystals with m. p. 173-174°, soon becoming lilac-colored and gradually turning darker. In moist air the salt rapidly absorbs moisture and darkens.

Found %: N 5.25. $C_{14}H_{20}O_2NCl$. Calculated %: N 5.20.

Picrate, recrystallized from aqueous alcohol, m.p. 148°.

Found %: N 12.18, 12.25. $C_{20}H_{22}O_9N_4$. Calculated %: N 12.15.

• The chloroplatinic acid was prepared from cut strips of platinum sheet, using the method of [10].

5. N-(p-Aminophenyl)-piperidine Hydrochloride. A mixture of 3.12 g of pyridine p-nitrochlorophenylate and 113 mg of catalyst in 100 ml of methyl alcohol was hydrogenated for 2 hours and 46 minutes. The hydrogen absorbed was 1564 ml (6 moles). During filtration the pale yellow solution of the salt, obtained after hydrogenation, first assumed a violet, and then a blue color. The dry residue (2.2 g) was decolorized with carbon and recrystallized twice from an alcohol-ether mixture to give colorless crystals with m. p. 199-200°.

Found %: N 13.13; Cl 16.73, 16.79. $C_{11}H_{17}N_2Cl$. Calculated %: N 13.18; Cl 16.71.

The Picrate was recrystallized from water, m.p. 132°.

Found %: N 17.25, 17.30. $C_{17}H_{17}O_7N_5$. Calculated %: N 17.33.

6. N-(p-Aminobiphenyl)-piperidine. A mixture of 0.565 g of pyridine p-aminochlorobiphenylate [8] and 200 mg of catalyst in 120 ml of alcohol was hydrogenated for 1.5 hours. The amount of hydrogen absorbed was 220 ml (3 moles). After removal of the catalyst by filtration the solution assumed a yellow color. The dry residue was a yellow powder (0.5 g). The salt could not be purified. A water solution of the salt was neutralized with 10% sodium hydroxide, and the free base was recrystallized from aqueous alcohol (1:1) to give a light colorless precipitate (0.15 g was obtained from 0.35 g of crude product).

Found %: N 11.46. $C_{17}H_{20}N_2$. Calculated %: N 11.11.

The hydrogenation of the decomposition product of the pyridine dye, a benzidine derivative [7] (I), X = NH_2, was run under similar conditions. A mixture of 0.33 g of the salt and 200 mg of catalyst in 120 ml of alcohol was hydrogenated for 1.5 hours. The hydrogen absorbed was 230 ml (3 moles). The dry residue (0.65 g) was washed several times with ether, and the ether extract was shown to contain traces of benzidine. The hydrogenation product proved to be difficultly soluble in water and alcohol, and its recrystallization (0.35 g) from water gave 0.13 g of silvery scales, which did not melt when heated but only charred gradually.

Found %: N 10.80, 10.84. $C_{29}H_{33}N_4Cl \cdot 2H_2O$. Calculated %: N 11.01.

Treatment of a water solution of 0.3 g of the hydrogenation product with 10% sodium hydroxide gave the free base and a dark tar. After recrystallization from aqueous alcohol the free base melted at 112°. Its mixed melting point with N-(p-aminobiphenyl)-piperidine was not depressed. Extraction of the tar, obtained in the treatment of the hydrogenation product with alkali, with hot ether yielded benzidine.

SUMMARY

1. Six N-aryl substituted pyridine salts were hydrogenated with Pt-catalyst in methyl alcohol at room temperature. These pyridine salts were: the chlorophenylate, the p-methyl-, p-methoxy-, p-carbethoxy- and p-nitrochlorophenylates, and the p-aminochlorobiphenylate derivative.

2. The hydrochlorides and picrates of the N-arylpiperidines were prepared and studied.

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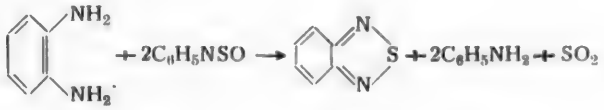
CHEMISTRY OF 2,1,3-THIADIAZOLE

III. REACTION OF AROMATIC o-DIAMINES WITH THIONYL CHLORIDE AND THIONYLANILINE*

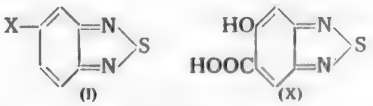
V. G. Pesin, A. M. Khaletsky, and Chzhao Chzi-chzhun

It is known that piazthiole can be obtained by the reaction of o-phenylenediamine with sulfur dioxide [2]; however, due to the difficulties associated in running it (heating in sealed tubes), this method possesses only theoretical interest. Of greater importance here is the Michaelis reaction [3], studied in detail by us earlier [1], and involving the reaction of o-phenylenediamine with thionyl chloride. It would seem that the formation of the given heterocycle from compounds with a high reactivity should proceed quite vigorously. Actually, as was shown by us [1], the cyclization proceeds quite slowly (12-15 hours), which can be explained by the formation of o-phenylenediamine hydrochloride, showing slight solubility in inert solvents (benzene, toluene); apparently, the slow formation of the heterocycle is determined by the low concentration of the free base. In the presence of tertiary bases (triethylamine, pyridine), as the experimental data revealed, the formation of benzo-2,1,3-thiadiazole proceeds with great vigor and is ended in 20-30 minutes with a yield of 85-90%.

4-Nitro-1,2-diaminobenzene, similar to o-phenylenediamine, also reacts with thionyl chloride, forming 5-nitrobenzo-2,1,3-thiadiazole in 90% yield. These data support our earlier statements that there are no major differences [1, 5] in the reaction of 1,2-phenylenediamine and 4-nitro-1,2-phenylenediamine with thionyl chloride, and refute the statement that 4-nitro-1,2-diaminobenzene is less reactive than the 3-nitro isomer in the formation of the thiadiazole ring [4]. The investigators explained this "lesser reactivity" of 4-nitro-1,2-diaminobenzene as being due to the "electrophilic influence of the nitro group in the 4 position," as it were, "preventing reconstruction of the π-electron cloud, necessary for closure of the thiadiazole ring." To overcome the indicated "lesser reactivity" the authors [4], in the preparation of 5-nitro-2,1,3-thiadiazole, heated 4-nitro-1,2-phenylenediamine with thionyl chloride for several hours at 127-130°, whereas, as we had shown, this reaction proceeds very easily and rapidly in the presence of tertiary amines. However, in the case where the o-phenylenediamine derivative contains reactive substituents, as for example, phenolic, carboxylic, sulfo, amino, sulfhydryl or similar groups, this reaction is apparently not applicable, and it is expedient to use thionylaniline. In the presence of the latter the reaction proceeds with exceeding ease, in some cases even at room temperature, giving arylthiadiazoles in a yield of 90% and better by the equation



This method was used by us to synthesize a large number of benzothiadiazole derivatives of general formula (I)



(I) (X)

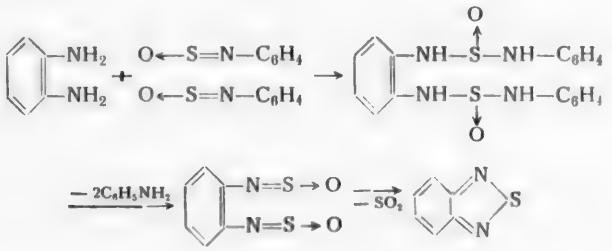
where X = NO_2 (II), CH_3 (III), OC_2H_5 (IV), Cl (V), Br (VI), $COOC_2H_5$ (VII), COOH (VIII), SO_3H (IX).

* The present investigation is a continuation of our earlier published papers under the name "Synthesis of Piazthiole (3,4-benzo-1,2,5-thiadiazole) and Its Derivatives" [1].

In addition, we obtained 5-hydroxybenzo-2,1,3-thiadiazole-6-carboxylic acid (X).

The obtained data permit the conclusion that the reaction between aromatic o-diamines and thionylaniline possesses a general character and is independent of both the nature and position of substituents.

As regards the mechanism of the reaction of thionylaniline with o-diamines, then here it can be postulated that the reaction proceeds in several stages, in part with the formation of addition products between the thionylaniline and the o-diamine, followed by the liberation of aniline and sulfur dioxide in accord with the scheme



Such a concept of the reaction mechanism emanates from the facts of reacting 1 mole of o-diamine with 2 moles of thionylaniline. In the case where o-phenylenediamine and thionylaniline are reacted in equimolar amounts the yield of benzo-2,1,3-thiadiazole drops to 46-48%, i. e., in half. It should also be mentioned that a red color is formed when thionylaniline is added to o-phenylenediamine or its derivatives, which disappears in measure with the liberation of sulfur dioxide and aniline.

The proposed reaction mechanism is quite clear from both the energy standpoint and the law of mass action; during cyclization, associated with the formation of a five-membered ring and the evolution of sulfur dioxide, the equilibrium is shifted to the right, as a result of which the process becomes irreversible.

EXPERIMENTAL

Thionylaniline and Benzo-2,1,3-thiadiazole were obtained by our earlier described method [5]; variation in the amounts of reactants, length of heating and in the medium employed gave the following results (Table 1).

TABLE 1

o-Phenylenediamine (in moles)	Thionylaniline in moles	Solvent	Amount of solvent (in ml)	Temperature	Reaction time (in min)	Yield (in %)
0.050	0.10	Benzene	40	80°	60	88.6
0.050	0.11	Benzene	40	80	30	90.0
0.050	0.11	Ethanol	50	80	30	86.0
0.025	0.10	Methanol	25	65	10	84.3
0.050	0.05	Benzene	40	80	30	46.0

As can be seen from the data in Table 1, when equimolar amounts of o-phenylenediamine and thionylaniline (in benzene medium) are used the yield of benzo-2,1,3-thiadiazole is reduced approximately in half.

For the preparation of benzo-2,1,3-thiadiazole and its derivatives by the reaction of o-diamines with thionyl chloride in the presence of tertiary bases (triethylamine, pyridine), see [5].

5-Nitrobenzo-2,1,3-thiadiazole (II). To 1.5 g of 4-nitro-1,2-diaminobenzene in 15 ml of benzene was added 3.1 g of thionylaniline. After heating for 3 hours on the water bath with constant stirring, followed by cooling, the obtained brown precipitate was filtered and washed with benzene. We obtained 0.9 g of substance with m. p. 124-126°; another 0.65 g was isolated from the mother liquor; total yield 1.6 g (88.8%). After recrystallization from carbon tetrachloride, m. p. 128°. The reaction was run under various conditions, in which connection the following results were obtained (Table 2).

TABLE 2

4-Nitro-1,2-diaminobenzene (in g)	Thionylaniline (in g)	Solvent	Amount of solvent (in ml)	Reaction time (in hrs)	Yield (in %)
3.8	7.5	Xylene	15	3	84.8
1.5	3.1	Toluene	10	3	90.0
1.5	3.1	Benzene	15	3	88.8
1.5	3.5	Ethanol	60	1	86.0
1.5	3.5	Methanol	15	1	82.0

The 4-nitro-1,2-diaminobenzene needed for the given synthesis was obtained by the reduction of 2,4-dinitroaniline. A mixture of 36 g of 2,4-dinitroaniline, 150 ml of methanol and 30 g of ammonium chloride was heated to the boil in a flask under reflux with stirring; to the hot mixture was added 110 g of sodium sulfide in 1 hour, the mixture boiled for 1 hour, cooled, the red precipitate separated, washed with water, heated with 300 ml of 4% hydrochloric acid, after separating the unreacted 2,4-dinitroaniline the filtrate was cooled to 60° and made alkaline with ammonia solution. The obtained red precipitate was separated, washed with water, and dried at 100°; m. p. 193-195° (yield 58%).

5-Methylbenzo-2,1,3-thiadiazole (III). A mixture of 23 g of p-tolulenediamine, 30 ml of toluene and 52 g of thionylaniline was heated on a boiling water bath; here the initially red-colored solution gradually decolorized, and sulfur dioxide was evolved. After heating for 1 hour the toluene was removed by distillation and the residue was acidified with 4% hydrochloric acid; the yellow oily liquid that separated here crystallized on cooling. After steam-distillation and drying we obtained 24.9 g (89%) of substance with m. p. 34°. Colorless needles, soluble in alcohol, ether, benzene and other organic solvents, and insoluble in water.

5-Ethoxybenzo-2,1,3-thiadiazole (IV). A mixture of 1.2 g of 4-ethoxy-1,2-phenylenediamine, obtained by the reduction of 3-nitrophenetidine with sodium sulfide in the presence of sulfur [6], 5 ml of toluene and 2 ml of thionylaniline was heated on a boiling water bath for 1 hour; here the precipitate went into solution and sulfur dioxide was evolved. The toluene was removed by distillation, the residue treated with hydrochloric acid until acid to congo, the obtained brownish-yellow precipitate separated, washed with dilute hydrochloric acid, then with water, and dried in a desiccator. We obtained 1.4 g (97%) of substance with m. p. 74-78°; after recrystallization from 70° alcohol, m. p. 76-77°. Yellow crystals, insoluble in water, and readily soluble in alcohol, ether and other organic solvents [7].

5-Chlorobenzo-2,1,3-thiadiazole (V). A mixture of 3.5 g of 4-chloro-1,2-phenylenediamine, obtained by the reduction of 4-chloro-2-nitroaniline with sodium sulfide [8], 5 ml of benzene and 7.3 g of thionylaniline was heated on a boiling water bath with constant stirring for 1 hour; here it was observed that the precipitate went into solution and sulfur dioxide was evolved. The benzene was removed from the reaction mixture, the residue treated with 4% hydrochloric acid until acid to congo, the obtained precipitate filtered, washed with water, and dried in a desiccator; 3.6 g (84.7%) of substance with m. p. 52-55° was obtained. Long, colorless needles, volatile with steam, insoluble in water, and readily soluble in alcohol, ether, benzene and other organic solvents, and in fatty oils.

Found %: C 42.53, 42.43; H 1.84, 1.69; N 15.57, 15.81; S 18.98, 18.63; Cl 20.71, 20.63. $C_6H_3N_2SCl$.
Calculated %: C 42.23; H 1.76; N 16.4; S 18.76; Cl 20.82.

5-Bromobenzo-2,1,3-thiadiazole (VI). A mixture of 3.7 g of 4-bromo-1,2-phenylenediamine, obtained by the reduction of 4-bromo-2-nitroaniline [9], 15 ml of toluene and 7.5 g of thionylaniline was heated on a boiling water bath in a flask under reflux with constant stirring. Here the precipitate dissolved, and the red-colored solution gradually became colorless. After heating for 1 hour the reaction mixture was evaporated, the residue acidified with hydrochloric acid, the precipitate filtered, washed with water, and dried between filter paper. We obtained 3.8 g (89%) of substance, m. p. 55-58°; after recrystallization from 60° alcohol, m. p. 61°. Colorless needles, insoluble in water, and soluble in alcohol, ether, benzene and other organic solvents.

Found %: C 33.14, 33.93; H 1.69, 1.49; N 12.40, 12.44; S 14.43, 14.92; Br 37.56, 37.84. $C_6H_3N_2SBr$. Calculated %: C 33.50; H 1.39; N 13.02; S 14.89; Br 37.18.

Ethyl Benzo-2,1,3-thiadiazole-5-carboxylate (VII). A mixture of 2.5 g of ethyl 3,4-diaminobenzoate, obtained by the reduction of 3-nitro-4-aminobenzoic acid with tin in the presence of alcoholic hydrogen chloride solution [10], and 2.8 g of thionylaniline in 15 ml of benzene was heated for 1 hour on the water bath. The benzene was removed by distillation, the residue treated with hydrochloric acid until acid to congo, then cooled, the obtained precipitate separated, washed with water, and dried in a desiccator. We obtained 2.85 g (95%) of substance with m. p. 57-58.5°. Long yellowish needles, insoluble in water, and soluble in alcohol, ether, benzene and other organic solvents.

Found %: C 52.59, 52.12; H 4.13, 4.27; N 13.27, 13.95; S 15.40, 15.42. $C_9H_8O_2N_2S$. Calculated %: C 51.92; H 3.85; N 13.46; S 15.38.

Benzo-2,1,3-thiadiazole-5-carboxylic acid (VIII). A mixture of 1 g of 3,4-diaminobenzoic acid, obtained by the reduction of 3-nitro-4-aminobenzoic acid with tin in the presence of concentrated hydrochloric acid [11], 2 ml of anhydrous alcohol and 1.9 g of thionylaniline was heated for 1 hour under reflux on a boiling water bath. The precipitate obtained on cooling was filtered, and after precipitation from alkaline solution with hydrochloric acid, was recrystallized from either alcohol or ethyl acetate. We obtained 1 g (85.6%) of substance with m. p. 200-206°, which after recrystallization from alcohol had m. p. 226°. Yellowish crystals, insoluble in water, and soluble in hot alcohol, ethyl acetate and alkalies. When the reaction was run in xylene the yield was 97%.

Found %: C 46.72, 47.03; H 2.13, 2.39; N 14.85, 15.05; S 17.78, 17.23. $C_7H_4O_2N_2S$. Calculated %: C 46.66; H 2.22; N 15.55; S 17.77.

Benzo-2,1,3-thiadiazole-5-sulfonic acid (IX). A suspension of 9 g of 3,4-diaminobenzenesulfonic acid, obtained by the reduction of 3-nitro-4-acetaminobenzenesulfonic acid with tin in the presence of 28% hydrochloric acid [12], and 45 ml of aniline was treated with 15 g of thionylaniline, and the red-colored reaction mixture was heated with constant stirring for 3 hours at 120°. The precipitate obtained on cooling was filtered, washed with ether, and dried at 100°; we obtained 13.6 g of substance with m. p. 220-223°. Investigation of the precipitate revealed that its water solution is easily diazotized and the resulting diazo compound couples with β-naphthol; treatment with alkali yields aniline. All of this indicated that the precipitate was an adduct (benzo-2,1,3-thiadiazole-5-sulfonic acid and aniline).

To obtain the free acid we dissolved 12 g of the aniline salt in 100 ml of water, neutralized with barium carbonate, evaporated the filtrate in vacuo to dryness, and decomposed the obtained 10.2 g of barium benzo-2,1,3-thiadiazole-5-sulfonate with dilute sulfuric acid. Concentration of the filtrate in vacuo and recrystallization of the residue from water gave 7.4 g of benzo-2,1,3-thiadiazole-5-sulfonic acid (88%, based on the aniline salt of the given acid). The free acid is a white crystalline powder, not melting at 300°, readily soluble in water and alkalies, and insoluble in alcohol and ether.

Found %: C 25.58, 25.55; H 1.25, 1.26; N 9.65, 9.68; S 22.51, 22.15. $C_6H_3O_3N_2S_2Ba_{0.5}$. Calculated %: C 25.38; H 1.06; N 9.82; S 22.56.

5-Hydroxybenzo-2,1,3-thiadiazole-6-carboxylic acid (X). A mixture of 1.5 g of 4,5-diaminosalicylic acid, obtained by the reduction of 4-amino-5(p-sulfamylphenylazo)salicylic acid with stannous chloride in the presence of concentrated hydrochloric acid [13], 15 ml of pyridine and 3 g of thionylaniline was heated with constant stirring for 1 hour at 60°. The reddish-yellow solution was cooled, acidified with 8% hydrochloric acid, the yellow-brown precipitate separated, washed with water, and dried at 100°. The yield of substance with m. p. 208-210° was 1.5 g (85.8%); after recrystallization from alcohol, m. p. 211.5°. Yellow crystalline powder, insoluble in cold water, slightly soluble in hot water, and soluble in alcohol. Treatment of its water solution with ferric chloride gives a brown-red color.

Found %: C 43.19, 43.54; H 2.45, 2.26; N 13.84, 13.80; S 16.51, 16.42. $C_7H_4O_3N_2S_3$. Calculated %: C 42.86; H 2.04; N 14.28; S 16.32.

SUMMARY

1. The reaction of o-phenylenediamine and other aromatic amines with thionyl chloride was studied, in which connection it was established: a) the reaction proceeds slowly due to the formation of the hydrochlorides of the corresponding o-diamines, which inhibits their reaction with thionyl chloride to form the thiadiazole ring; b) the reaction is both vigorous and rapid in the presence of tertiary organic bases (triethylamine, pyridine) and here the yields are of the order of 85-90%.

2. The reaction of aromatic o-diamines with thionylaniline was studied, in which connection it was shown that here in a number of cases reaction is both vigorous and rapid even at room temperature, resulting in the formation of the corresponding benzo-2,1,3-thiadiazoles in up to 98% yield.

3. It was shown that the reaction of aromatic o-diamines with thionyl chloride or with thionylaniline can serve for the identification of o-diamines.

4. It was found, contrary to literature data, that electrophilic substituents in the 4 position (nitro group, etc.) do not prevent the reaction of aromatic o-diamine with thionyl chloride.

5. Improved methods were developed for the synthesis of thionylaniline and some of the intermediate products (4-chloro-2-nitroaniline, 4-ethoxy-1,2-phenylenediamine, etc.), used for the synthesis of benzothiadiazole derivatives.

6. The previously unknown 5-chloro- and 5-bromobenzo-2,1,3-thiadiazoles, benzo-2,1,3-thiadiazole-5-carboxylic acid and its ethyl ester, benzo-2,1,3-thiadiazole-5-sulfonic acid and 5-hydroxybenzo-2,1,3-thiadiazole-6-carboxylic acid were synthesized.

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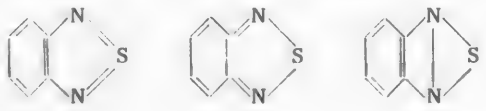
CHEMISTRY OF 2,1,3-THIADIAZOLE

IV. CHLORINATION AND BROMINATION OF BENZO-2,1,3-THIADIAZOLE

V. G. Pesin, A. M. Khaletsky, and Chzhao Chzhi-chzhun

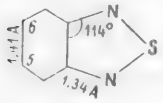
The structure of benzo-2,1,3-thiadiazole can be depicted by several formulas.



(I) (II) (III)

From the viewpoint of the strain theory it must be assumed that structure (III) is not very probable.

In addition, such a structure is refuted by the data of Luzzati [1], who studied the crystal structure and determined the interatomic distances and valence angles of benzo-2,1,3-thiadiazole. He found the valence angles between the C—C—N bonds to be equal to 114°, the distance between the carbon and nitrogen atoms to be equal to 1.34 A, and the distance between the carbon atoms in the 5,6 positions to be equal to 1.41 A, which can be schematically depicted in the following manner.

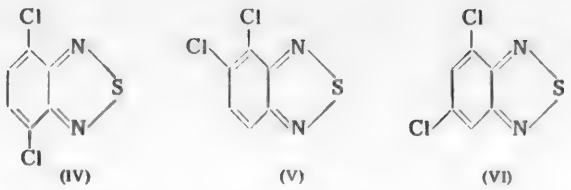


From these data it follows that the distance between the nitrogen atoms in the benzo-2,1,3-thiadiazole molecule is equal to 2.94 A, whereas if benzo-2,1,3-thiadiazole had the (III) structure, then the distance between the nitrogen atoms would not exceed 1.45-1.48 A [2].

As regards structures (I) and (II), then here the existing experimental data still do not permit making a choice between them. The synthesis of benzo-2,1,3-thiadiazole and its chemical properties point to structure (I) [3]; the measurement data obtained for the interatomic distances can apply to either structure (I) or (II). The studies of Hill and Sutton [4] are of interest in this connection; they showed that based on a measurement of the dipole moments of benzo-2,1,3-thiadiazole and benzo-2,1,3-selenadiazole the former most probably has the (II) structure, while for the latter either structure is equally probable.

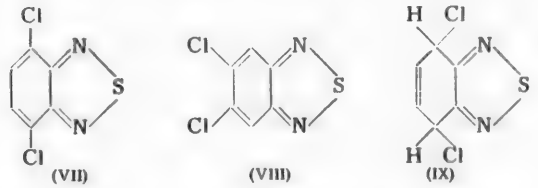
L. S. Efros and R. M. Levit [3] assign structure (II) to benzo-2,1,3-thiadiazole, in this connection without giving suitable experimental data (proof of the presence of unsaturated bonds, etc.). At the same time, the reactions dealing with the aromatic character of the heterocycle (nitration, etc.) do not evoke any doubt; however, as regards the (II) structure, then its proof is associated with establishing the presence of the above-mentioned unsaturated bonds. Meanwhile, according to the data of the mentioned authors, "piazthiole does not decolorize bromine water; it fails to react with halogens in the absence of catalysts and does not give addition products with substances of the H—A type," "the chlorination of piazthiole proceeds only when chlorine is passed through the molten product in the presence of iron filings. The reaction fails to go in the absence of catalysts; when chlorinated piazthiole behaves like ordinary aromatic compounds."

L. S. Efros and R. M. Levit passed chlorine into molten benzo-2,1,3-thiadiazole at 60° in the presence of iron filings until the increase in weight corresponded to the monchloro derivative and obtained in 4.9% yield a substance with m. p. 57.5°, for which they assume the structure of (IV).



(IV) (V) (VI)

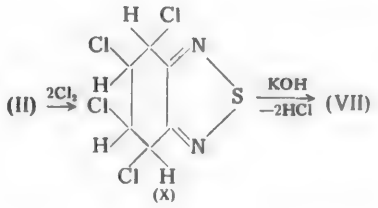
However, based on its melting point, the latter compound (IV) does not correspond to any of the four possible dichloro derivatives of benzo-2,1,3-thiadiazole, predicted by the structure theory, and synthesized by us (V-VIII).



(VII) (VIII) (IX)

The assumption remains that the dichloro derivative obtained by the indicated authors is a partially hydrogenated derivative of dichlorobenzo-2,1,3-thiadiazole (IX).

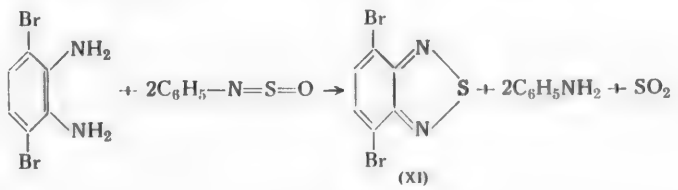
The studies made by us revealed that, contrary to the statements of the authors [3], benzo-2,1,3-thiadiazole readily adds chlorine with the evolution of heat, both in the presence and in the absence of catalysts (iron filings); the reaction proceeds in the molten state and in organic solvents (dichloroethane, chloroform, etc.). The chlorination product is a clear oily liquid, gradually solidifying; based on its analysis, the purified product is tetrachlorotetrahydrobenzo-2,1,3-thiadiazole (X), and when treated with alcoholic potassium hydroxide solution it is converted into 4,7-dichlorobenzo-2,1,3-thiadiazole (VII), the structure of which was shown by the counter synthesis from 3,6-dichloro-1,2-diaminobenzene and thionylaniline. These data permit depicting the reaction of benzo-2,1,3-thiadiazole with chlorine and the cleavage of hydrogen chloride in the following manner



(II) $\xrightarrow{2Cl_2}$ (X) $\xrightarrow[-2HCl]{KOH}$ (VII)

From the mixture of several stereoisomeric tetrachloro derivatives, predicted by the structure theory, we were able by fractional crystallization from alcohol to isolate two individual crystalline substances with m. p. 123-124° and 82°.

The reaction of benzo-2,1,3-thiadiazole with bromine is similar to its reaction with chlorine, and here also the bromination product when treated with alcoholic potassium hydroxide solution is converted into 4,7-dibromobenzo-2,1,3-thiadiazole (XI). The structure of the latter was shown by the counter synthesis from 3,6-dibromo-1,2-phenylenediamine and thionylaniline



(XI)

To verify our theory regarding the structure of the substance obtained by L. S. Efros and R. M. Levit [3] in the chlorination of benzo-2,1,3-thiadiazole, we ran the chlorination of the latter with stoichiometric amounts of chlorine (a weight increase corresponding to two chlorine atoms). Here after vacuum-distillation we isolated, besides unreacted benzo-2,1,3-thiadiazole, the above-mentioned tetrachloro derivative (X) and a viscous liquid, which when stored for a year failed to crystallize. Treatment of the latter with alcoholic potassium hydroxide solution gave 4,7-dichlorobenzo-2,1,3-thiadiazole (VII).

These data permit the assumption that apparently the first reaction here is the addition of two chlorine atoms to the benzo-2,1,3-thiadiazole with a shift of the double bond, and then the addition of another two chlorine atoms in accord with the scheme: (II) $\xrightarrow{Cl_2}$ (IX) $\xrightarrow{Cl_2}$ (X).

Apparently, the second stage of the reaction proceeded so vigorously under our conditions that it proved impossible to limit the process only to the first stage.

Some other benzo-2,1,3-thiadiazole derivatives, and also 1',2'-naphtho-2,1,3-thiadiazole, enter into the addition reaction with chlorine and bromine [5].

As a result, the experimental data clearly show that the above-mentioned statements of L. S. Efros and R. M. Levit that benzo-2,1,3-thiadiazole is incapable of addition reactions, and reacts with chlorine only in the presence of a catalyst, are incorrect.

The halogenation (chlorination, bromination) of benzo-2,1,3-thiadiazole and the dehydrochlorination (dehydrobromination) of its tetrahalo derivatives is most easily explained if the (II) structure is assigned to benzo-2,1,3-thiadiazole. Its stability and aromatic properties can be explained on the basis of the reaction and subsequent sharing of π-electrons. In addition, it is possible to explain the given structure on the basis of the substitution direction observed in certain cases, for example, in nitration, sulfonation, etc. As regards the final solution to the problem of the structure of benzo-2,1,3-thiadiazole, then this is the subject of further studies.

EXPERIMENTAL

Chlorination of Benzo-2,1,3-thiadiazole (in the presence of iron). Molten benzo-2,1,3-thiadiazole (4.5 g) with m. p. 42° was saturated at 60° with chlorine in the presence of 0.1 g of iron turnings. We obtained 9 g of thick yellow liquid, which failed to solidify on long storage (more than 1 year), and which was readily soluble in ether, alcohol and benzene. Treatment of the chlorinated product with 10% alcoholic potassium hydroxide solution gave a substance with m. p. 181-182.5°. The mixed melting point with authentic 4,7-dichlorobenzo-2,1,3-thiadiazole was not depressed.

The chlorinated product was studied further as follows: 35 g of chlorinated benzo-2,1,3-thiadiazole was heated with 50 ml of alcohol with stirring, and after cooling the alcohol solution was separated from the oily liquid; cooling of the alcohol solution in a mixture of ice and salt gave 7.7 g (22%) of crystals, which after recrystallization from alcohol had m. p. 120-124°. The substance was obtained as white needles, soluble in alcohol, chloroform, dichloroethane and benzene, slightly soluble in petroleum ether, and insoluble in water. The substance is tetrachlorotetrahydro-2,1,3-thiadiazole.

Found %: C 25.95, 26.10; H 1.45, 1.62; N 10.38, 10.05; S 11.30, 11.63; Cl 51.44, 51.68. $C_6H_4N_2Cl_4S$. Calculated %: C 25.90; H 1.44; N 10.07; S 11.51; Cl 51.08.

From the oily liquid after heating with 50 ml of alcohol and subsequent cooling we isolated 1.4 g of crystalline substance with m. p. 82°, soluble in alcohol, chloroform and benzene, slightly soluble in petroleum ether, and insoluble in water.

Found %: C 26. 68, 25.90; H 1.66, 1.47; N 10.23, 10.06; S 11.87, 11.76; Cl 52.02, 51.90. $C_6H_4N_2Cl_4S$. Calculated %: C 25.90; H 1.44; N 10.07; S 11.51; Cl 51.08.

On the basis of the study data the substances with m. p. 120-124° and 82° correspond to the same composition, and they can be considered to be isomers of tetrachlorotetrahydro-2,1,3-thiadiazole. Subsequent investigation of the filtrate, mixed with chloroform, for the purpose of isolating other stereoisomers, using the method of chromatographic adsorption on aluminum oxide, failed to give any definite results.

Chlorination of benzo-2,1,3-thiadiazole (in the absence of iron). Chlorine was passed into a melt of 13.6 g of benzo-2,1,3-thiadiazole at 60° to a weight increase of 7.1 g (corresponding to the introduction of two chlorine atoms); the obtained yellow oily substance was distilled; here the following four fractions were isolated: 1st, b. p. up to 140° (20-30 mm), 5 g, m. p. 42-44°; does not depress the melting point when mixed with benzo-2,1,3-thiadiazole; 2nd, b. p. 141-150° (20-30 mm), 2 g; represents a clear oily liquid, failing to crystallize when stored; treatment with alcoholic potassium hydroxide solution gave a substance with m. p. 175-178°, not depressing the melting point when mixed with 4,7-dichlorobenzo-2,1,3-thiadiazole; 3rd, b. p. 151-185° (20-30 mm), 3.5 g; represents an oily liquid that crystallized on standing; after recrystallization from alcohol, m. p. 75-82°; its mixed melting point with tetrachlorotetrahydrobenzo-2,1,3-thiadiazole (m. p. 82°) was not depressed; 4th, b. p. 186-195° (20-30 mm), 4 g; represents an oily liquid that crystallized rapidly; after recrystallization from alcohol, m. p. 175-178°; its mixed melting point with 4,7-dichlorobenzo-2,1,3-thiadiazole was not depressed. As a result, the same products were obtained independent of whether the reaction was run in the presence or absence of a catalyst.

4,5-Dichlorobenzo-2,1,3-thiadiazole (V). To 4.5 g of mixed isomeric dichlorodiaminobenzenes, obtained by the nitration of 2,3-dichloronitrobenzene with m. p. 61° and subsequent reduction of the 2,3-dichloro-1,2-dinitrobenzenes [6], and 10 ml of benzene was gradually added 4.5 g of thionylaniline (b. p. 198-200°), and the reaction mixture was stirred with heating on the water bath for 30 minutes. The benzene was removed by distillation, the residue treated with 4% hydrochloric acid, the mixture filtered, and the precipitate washed with water and dried in a vacuum-desiccator. Recrystallization from alcohol gave 4,5-dichlorobenzo-2,1,3-thiadiazole with m. p. 112-113° (28.8%, based on the mixture of dichlorodiaminobenzenes), obtained as white needle crystals, insoluble in water, and soluble in alcohol and chloroform.

Found %: C 35.48, 35.28; H 1.43, 1.29; N 13.82, 13.76; S 15.19, 15.53; Cl 34.74, 34.51. $C_6H_2N_2Cl_2S$. Calculated %: C 35.12; H 0.97; N 13.66; S 15.68; Cl 34.63.

5,6-Dichlorobenzo-2,1,3-thiadiazole (VIII). To a suspension of 3.98 g of 4,5-dichloro-1,2-phenylenediamine, obtained by the reduction of 3,4-dichloro-1,2-dinitrobenzene with tin in the presence of concentrated hydrochloric acid [7], and 10 ml of benzene was gradually added with constant stirring 7 g of thionylaniline. After heating on the water bath for 30 minutes the red-colored reaction mixture gradually decolorized, and sulfur dioxide was evolved. After removal of the benzene by distillation the precipitate was filtered, washed with benzene and dried in a desiccator. We obtained 4.05 g (88.3%) of substance with m. p. 112-113°, being white crystals, soluble in alcohol, benzene and chloroform, and insoluble in water.

Found %: C 35.54, 35.20; H. 1.32, 1.35; N 13.97, 13.80; S 15.43, 15.22; Cl 34.43, 34.43. $C_6H_2N_2Cl_2S$. Calculated %: C 35.12; H 0.97; N 13.66; S 15.68; Cl 34.63.

On the basis of the study data the substance with m. p. 112-113° has the structure of 5,6-dichlorobenzo-2,1,3-thiadiazole.

5,7-Dichlorobenzo-2,1,3-thiadiazole (VI). To 2 g of 4,6-dichloro-1,2-phenylenediamine (m. p. 60.5°), obtained by the reduction of 4,6-dichloro-2-nitroaniline (m. p. 97-99°) with tin in the presence of concentrated hydrochloric acid [8], and 10 ml of benzene was gradually added 3.5 g of thionylaniline; the red-colored reaction mixture was heated on the water bath with constant stirring for 30 minutes. After removal of the benzene by distillation the residue was acidified with 4% hydrochloric acid until acid to congo, and the obtained white precipitate was filtered and dried in a desiccator; we obtained 2.3 g (99%) of substance, which after recrystallization from 70° alcohol had m. p. 97-97.7°. The substance was obtained as white needles, soluble in alcohol, ether, chloroform and dichloroethane, and insoluble in water. It corresponds to 5,7-dichlorobenzo-2,1,3-thiadiazole.

Found %: C 35.46, 35.69; H 1.14, 1.46; N 13.85, 13.69; S 15.41, 15.67; Cl 34.63, 34.63. $C_6H_2N_2Cl_2S$. Calculated %: C 35.12; H 0.97; N 13.66; S 15.68; Cl 34.63.

4,7-Dichlorobenzo-2,1,3-thiadiazole (VII). To a suspension of 3,6-dichloro-1,2-phenylenediamine (m. p. 95-97°), obtained by the reduction of 1,4-dichloro-2,3-dinitrobenzene (m. p. 103°) with tin in the presence of concentrated hydrochloric acid [7], and 5 ml of benzene was gradually added, with constant stirring, 3.8 g of thionylaniline. After heating on the water bath for 30 minutes the decolorized reaction mass, originally red-

colored, was cooled, the precipitate filtered, washed with benzene, and then recrystallized from alcohol to give 2.05 g of substance with m. p. 181-182.5°. The latter was obtained as colorless needle-like crystals, insoluble in water, slightly soluble in alcohol, more readily soluble in hot alcohol, and soluble in chloroform and dichloroethane.

Found %: C 35.43, 35.81; H 1.22, 1.35; N 13.52, 13.82; S 15.21, 15.68; Cl 35.01, 34.80. $C_6H_2N_2Cl_2S$. Calculated %: C 35.12; H 0.97; N 13.66; S 15.68; Cl 34.63.

On the basis of the study data the substance with m. p. 181-182.5° has the structure of 4,7-dichlorobenzo-2,1,3-thiadiazole.

Bromination of benzo-2,1,3-thiadiazole. To 9 g of molten benzo-2,1,3-thiadiazole (m. p. 42°) at 65-77° in 25 minutes with constant stirring was added 32 g of bromine; here a rise in temperature was observed. After all of the bromine had been added the reaction mixture was heated for 1 hour at the boil, and the solid mass obtained on cooling was allowed to stand in the air to evaporate excess bromine. The yield of yellowish substance was 28.85 g (95.6%), which after recrystallization from alcohol was obtained as colorless crystals with m. p. 152°, readily soluble in benzene, carbon tetrachloride, acetone and acetic acid, and less soluble in alcohol.

Found %: N 6.19, 6.29. $C_6H_4N_2BrS$. Calculated %: N 6.14.

The substance is tetrabromotetrahydro-2,1,3-thiadiazole.

4,7-Dibromobenzo-2,1,3-thiadiazole. A mixture of 1 g of the above described brominated product with m. p. 142°, 20 ml of alcohol and a solution of 0.32 g of potassium hydroxide in 1 ml of water was heated at the boil for 1 hour; cooling and dilution with water gave 0.52 g (80%) of substance, which after recrystallization from alcohol had m. p. 184-185°. Its mixed melting point with the 4,7-dibromobenzo-2,1,3-thiadiazole, obtained from 3,6-dibromo-1,2-diaminobenzene and thionylaniline, was not depressed.

Found %: N 9.88, 9.61. $C_6H_2N_2Br_2S$. Calculated %: N 9.52.

On the basis of the study data it follows that four bromine atoms are added when benzo-2,1,3-thiadiazole is brominated, and that the subsequent treatment of the brominated product with alcoholic potassium hydroxide solution results in the cleavage of two molecules of hydrogen bromide. The 3,6-dibromo-1,2-diaminobenzene was obtained by the reduction of 3,6-dibromo-1,2-dinitrobenzene (m. p. 157-160°) with tin in the presence of concentrated hydrochloric acid [7], while the 3,6-dibromo-1,2-dinitrobenzene was obtained by the Austen method [9], involving the nitration of 1,4-dibromobenzene.

4,7-Dibromobenzo-2,1,3-thiadiazole was synthesized by heating 1 g of 3,6-dibromo-1,2-diaminobenzene (m. p. 184-185°) with 1.2 g of thionylaniline and 3 ml of benzene at 80-90° for 30 minutes.

SUMMARY

1. The reaction of benzo-2,1,3-thiadiazole with halogens (chlorine, bromine) was studied; here it was found that 4 halogen atoms are added with vigor to form the tetrahalo derivative. Of the different isomeric tetrachloro derivatives predicted by the structure theory we isolated two of the isomers as crystalline compounds with m. p. 120-124° and 82°. The ability shown by benzo-2,1,3-thiadiazole to add four halogen atoms is evidence of its unsaturated character; this reaction demonstrated the error of the conclusions made by L. S. Efros and R. M. Levit that benzo-2,1,3-thiadiazole is incapable of adding halogens (chlorine).

2. It was shown that when treated with alcoholic potassium hydroxide solution the tetrahalotetrahydro derivatives of benzo-2,1,3-thiadiazole lose two molecules of hydrogen halide with the respective formation of either 4,7-dichloro- or 4,7-dibromobenzo-2,1,3-thiadiazole.

3. All of the different isomeric dichloro derivatives of benzo-2,1,3-thiadiazole predicted by the structure theory were synthesized; here it was shown that the substance described by L. S. Efros and R. M. Levit is not included among them. The reaction mechanism proposed by us for the halogenation of benzo-2,1,3-thiadiazole permits assuming that the dichloro derivative isolated by the indicated authors is actually a dichlorodihydrobenzo-2,1,3-thiadiazole.

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PROPERTIES OF FURANIDINO-(3,4)-IMIDAZOLES

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In previous studies two of us had shown that the reaction of 3,4-diketones of the furanidine series gives in good yields condensed heterocyclic compounds, containing both the imidazole and furanidine rings [1, 2]. To answer the question of the influence exerted by the furanidine ring on the specific properties of the imidazole ring, entering into the composition of condensed furanidino-(3,4)-imidazole systems, we present in this paper a detailed study of the chemical properties of imidazoles with a similar structure.

It is known that the imidazoles are monoacidic bases and form stable crystalline salts when treated with acids [3]. At the same time the imidazoles are monobasic acids [4]. Using the potentiometric method we measured the basicity constants and the acidity constants of four furanidino-(3,4)-imidazoles. The data obtained by us, and also the dissociation constants of aniline and phenol, measured under the same conditions [5], and the dissociation constants of imidazole and benzimidazole [3, 4, 6], are given in the table. From these data it follows that the furanidino-(3,4)-imidazoles are stronger bases than aniline, and weaker acids than phenol; they are somewhat weaker bases than imidazole, and show the same order of basicity as benzimidazole.

The similarity with imidazole and the greater closeness to benzimidazole also appears in the chemical reactions of the furanidino-(3,4)-imidazoles studied by us. The hydrochlorides of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole and 4,4,6,6,-bistetramethylfuranidino-(3,4)-imidazole are crystalline substances, not decomposing when boiled in ethyl alcohol for many hours. The same as all imidazole compounds, 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole gives the methiodide in quantitative yield.

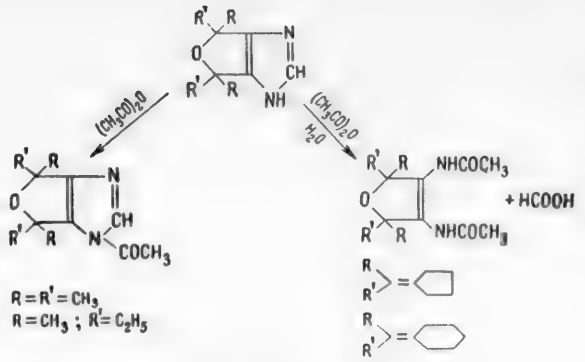
Characteristic for all imidazoles is the reaction with acid anhydrides and chlorides, which, depending on the conditions, leads either to N-acylated imidazoles or, as the result of opening the imidazole ring, to diacylated diamines [7]. We established that the furanidino-(3,4)-imidazoles are readily acylated; however, the obtained N-acylated derivatives are unstable and when exposed to atmospheric moisture for several days they suffer hydrolysis with the formation of the original imidazole. When the furanidino-(3,4)-imidazoles are boiled for a long time with a large excess of acetic anhydride, followed by decomposition of the mixture with boiling water, the imidazole ring is opened with the formation of 3,4-diacetamino-2,5-dihydrofurans.

The following were obtained in this manner in 70-85% yields: 3,4-diacetamino-2,2,5,5-tetramethyl-2,5-dihydrofuran, 3,4-diacetamino-2,5-dimethyl-2,5-diethyl-2,5-dihydrofuran, 3,4-diacetamino-2,2,5,5-bistetramethylene-2,5-dihydrofuran and 3,4-diacetamino-2,2,5,5-bispentamethylene-2,5-dihydrofuran.

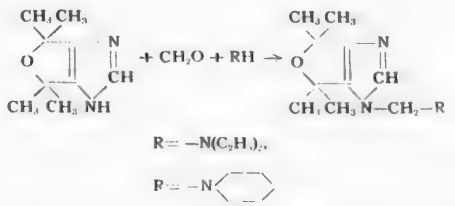
The benzoylation of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole by the Schotten-Baumann method gave 3,4-dibenzoylamino-2,2,5,5-tetramethyl-2,5-dihydrofuran.

Attempts to hydrogenate the diacylated diamines of the 2,5-dihydrofuran series with hydrogen in the presence of skeletal nickel or platinum at atmospheric pressure gave negative results – the hydrogenation did not go. (See diagram on following page).

It is known that benzimidazole can be aminomethylated by the Mannich method, forming 1-dialkylaminomethylbenzimidazoles [8]. It was shown by us that 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole reacts with formaldehyde and diethylamine or piperidine, giving,respectively, 1-diethylaminomethyl-4,4,6,6-tetramethyl-



furanidino-(3,4)-imidazole and 1-piperidinomethyl-4,4,6,6-tetramethylfuranidino-(3,4)-imidazole.



The imidazole ring is extremely resistant to the action of oxidizing agents: according to the data of Bamberger, in the oxidation of imidazole the benzene ring suffers decomposition and imidazole-4,5-dicarboxylic acid is formed [9]. We oxidized 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole and 4,4,6,6-bistetramethylenefuranidino-(3,4)-imidazole with potassium dichromate in sulfuric acid. The oxidation product was imidazole-4,5-dicarboxylic acid, which was formed as the decomposition result of the furanidine ring of the furanidino-(3,4)-imidazole.

EXPERIMENTAL

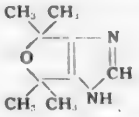
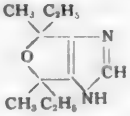
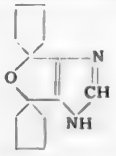
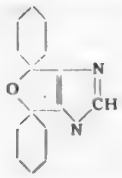
Measurement of the dissociation constants. To calculate the dissociation constants we measured the solution pH of various furanidino-(3,4)-imidazoles in 80% ethyl alcohol. An LP-4 potentiometer with glass electrode was used to make the measurements. The acidity constants (K_a) and basicity constants (K_b) were calculated by means of Formulas (1) and (2) [10].

$$K_a = \frac{[H^+]\left\{[Na^+] + [H^+] - \frac{K_{W_1}}{[H^+]}\right\}}{M - \left\{[Na^+] + [H^+] - \frac{K_{W_2}}{[H^+]}\right\}} \qquad (1)$$

$$K_b = \frac{K_W\left\{[Cl^-] - [H^+] + \frac{K_{W_1}}{[H^+]}\right\}}{[H^+]\left\{M - \left|[Cl^-] - [H^+] + \frac{K_{W_2}}{[H^+]}\right|\right\}}, \qquad (2)$$

where K_W is the ionization constant of water, K_{W_1} is the ionization constant of the solvent, equal to $1 \cdot 10^{-16}$, and M is the molality of the solution, equal to 0.005.

A 0.005 M aqueous alcohol solution of the furanidino-(3,4)-imidazole was neutralized to the extent of 30, 50 and 70% with 0.05 N hydrochloric acid and the pH of the obtained solutions was measured with a glass electrode at 20°. The calculated pK_b values for the different degrees of neutralization did not differ by more than 0.05. The acidity constants were determined in a similar manner, but here 0.05 N sodium hydroxide solution was used for the neutralization. The obtained results are summarized in the table.

Name and formula	pK_b	pK_a
4,4,6,6-Tetramethylfuranido-(3,4)-imidazole 	9.08	13.02
4,6-Dimethyl-4,6-diethylfuranido-(3,4)-imidazole 	11.76	—
4,4,6,6-Bistetramethylenefuranidino-(3,4)-imidazole 	9.32	12.88
4,4,6,6-Bispentamethylenefuranidino-(3,4)-imidazole 	8.07	12.94
Aniline [5]	10.14	—
Phenol [5]	—	11.33
Imidazole [3]	7.05	—
Benzimidazole [6]	8.6	12.7

4,4,6,6-Tetramethylfuranidino-(3,4)-imidazole hydrochloride. Dry hydrogen chloride was passed into a solution of 0.6 g (0.0036 mole) of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole in 13 ml of anhydrous alcohol. The yield of hydrochloride with m. p. 203-203.5° (from alcohol) was 0.6 g (76%).

Found %: C 53.25, 53.04; H 7.19, 7.05; N 14.11, 13.95. $C_9H_{15}ON_2Cl$. Calculated %: C 53.33; H 7.46; N 13.82.

4,4,6,6-Tetramethylfuranidino-(3,4)-imidazole methiodide. A mixture of 0.8 g (0.005 mole) of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole, 0.7 g (0.005 mole) of methyl iodide and 10 ml of absolute methyl alcohol was heated in a sealed tube for 3 hours on a boiling water bath. After vacuum-distillation of the alcohol the reaction product was recrystallized from anhydrous acetone. Quantitative yield, m. p. 191°.

Found %: C 38.56, 38.52; H 5.80, 5.79. $C_{10}H_{17}ON_2I$. Calculated %: C 38.97; H 5.56.

1-Acetyl-4,4,6,6-tetramethylfuranidino-(3,4)-imidazole. A mixture of 0.9 g (0.0054 mole) of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole and 3.1 g (0.03 mole) of acetic anhydride was boiled under reflux for 20 minutes. After vacuum-distillation of the unchanged acetic anhydride the reaction product was recrystallized from petroleum ether, m. p. 111-112.5°. Yield 0.9 g (80%).

Found %: C 63.26, 63.10; H 7.76, 7.73; N 13.38, 13.26. $C_{11}H_{16}O_2N_2$. Calculated %: C 63.44; H 7.74; N 13.45.

When exposed to atmospheric moisture for 7 days the compound suffered hydrolysis with the formation of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole with m. p. 288°; its mixed melting point with authentic 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole was not depressed.

3,4-Diacetamino-2,2,5,5-tetramethyl-2,5-dihydrofuran. A mixture of 1.7 g (0.01 mole) of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole and 17 g (0.16 mole) of acetic anhydride was boiled under reflux for 2 hours, and then it was poured into 50 ml of water and evaporated nearly to dryness; this operation was repeated until the odor of acetic anhydride was no longer noted in the residual crystalline mass. The latter after washing with a small amount of cold water was dried; we obtained 1.6 g (66.5%) of reaction product with m. p. 304-305° (from alcohol).

Found %: C 59.98, 59.98; H 8.47, 8.47; N 11.73, 11.94. $C_{12}H_{20}O_3N_2$. Calculated %: C 59.97; H 8.39; N 11.69.

3,4-Diacetamino-2,5-dimethyl-2,5-diethyl-2,5-dihydrofuran. From 1.0 g (0.005 mole) of 4,6-dimethyl-4,6-diethylfuranidino-(3,4)-imidazole and 17 g (0.16 mole) of acetic anhydride we obtained, in the same manner as described above, 1.2 g (85%) of reaction product, m. p. 261.5° (from alcohol).

Found %: C 62.68, 62.58; H 9.13, 9.08. $C_{14}H_{24}O_3N_2$. Calculated %: C 62.61; H 9.03.

3,4-Diacetamino-2,2,5,5-bistetramethylene-2,5-dihydrofuran. From 0.2 g (0.001 mole) of 4,4,6,6-bistetramethylenefuranidino-(3,4)-imidazole and 10 g (0.1 mole) of acetic anhydride we obtained 0.2 g (69%) of reaction product with m. p. 345° (from alcohol).

Found %: C 65.97, 65.92; H 8.59, 8.68. $C_{16}H_{24}O_3N_2$. Calculated %: C 65.71; H 8.30.

3,4-Diacetamino-2,2,5,5-bispentamethylene-2,5-dihydrofuran. From 0.5 g (0.002 mole) of 4,4,6,6-bispentamethylenefuranidino-(3,4)-imidazole and 8.5 g (0.08 mole) of acetic anhydride we obtained 0.55 g (91%) of reaction product with m. p. 320° (from alcohol).

Found %: C 67.71, 67.51; H 9.04, 8.95. $C_{18}H_{28}O_3N_2$. Calculated %: C 67.47; H 8.81.

4,5-Dibenzoylamino-2,2,5,5-tetramethyl-2,5-dihydrofuran. To a mixture of 1.6 g (0.01 mole) of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole, 40 ml of water and 6 ml of 30% sodium hydroxide solution was added in drops, with ice cooling, 5 g (0.35 mole) of benzoyl chloride. The white precipitate was separated and washed several times with hot 20% sodium hydroxide solution. We obtained 1.5 g (41%) of reaction product, m. p. 230.5° (from alcohol).

Found %: C 72.88, 72.73; H 6.85, 6.78. $C_{22}H_{24}O_3N_2$. Calculated %: C 72.50; H 6.64.

1-Diethylaminomethyl-4,4,6,6-tetramethylfuranidino-(3,4)-imidazole. To a solution of 1.0 g (0.006 mole) of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole in 50 ml of ethyl alcohol was added 1.0 g (0.014 mole) of diethylamine and 1.5 ml (0.02 mole) of 40% formalin. The reaction mixture was boiled under reflux for 4 hours, the alcohol was vacuum-distilled, and the residue was treated with 30 ml of anhydrous benzene. After vacuum-distillation of the benzene (to remove the water) the residue was recrystallized from petroleum ether. We obtained 0.6 g (40%) of reaction product, m. p. 170°.

Found %: C 66.90, 67.12; H 9.34, 9.36; N 16.97. $C_{14}H_{25}ON_3$. Calculated %: C 66.87; H 10.04; N 16.72.

1-Piperidinomethyl-4,4,6,6-tetramethylfuranidino-(3,4)-imidazole. A mixture of 1 g (0.006 mole) of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole, 1 g (0.012 mole) of piperidine and 1 ml (0.013 mole) of 40% formalin was heated under reflux for 3 hours on a boiling water bath, then 50 ml of anhydrous benzene was added, and the mixture was vacuum-distilled to remove the water. We obtained 0.6 g (38%) of reaction product, m. p. 219° (from acetone).

Found %: C 67.92, 67.83; H 9.15, 9.08; N 15.97, 16.05. $C_{15}H_{25}ON_2$. Calculated %: C 68.38; H 9.58; N 15.95.

Oxidation of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole. To a mixture of 0.9 g (0.005 mole) of 4,4,6,6-tetramethylfuranidino-(3,4)-imidazole, 10 ml of concentrated sulfuric acid and 8 ml of water heated to 90°, was added in small portions, with vigorous stirring, 5 g of potassium dichromate at such a rate that the temperature of the mixing held at 90-95°. After all of the potassium dichromate had been added the reaction mixture was stirred for another 10-15 minutes, and then it was poured into 80 ml of cold water. The precipitate was separated and washed several times with cold water. The imidazole-3,4-dicarboxylic acid was purified by precipitation with hydrochloric acid from alkaline solution; m. p. 290° (with decomposition); literature [11]: m. p. 290° (with decomposition).

Oxidation of 4,4,6,6-bistetramethylenefuranidino-(3,4)-imidazole. The oxidation of 4,4,6,6-bistetramethylenefuranidino-(3,4)-imidazole with potassium dichromate under the above described conditions gave imidazole-4,5-dicarboxylic acid with m.p. 290° (with decomposition).

SUMMARY

Furanidino-(3,4)-imidazoles, whose condensed system contains both furanidine and imidazoline rings, are completely analogous to the alkyl- and benzimidazoles in their properties: when treated with acids they give salts; when reacted with methyl iodide they form methiodides; when reacted with acetic anhydride they give either N-acetylfuranidino-(3,4)-imidazoles or N-diacetylated diamines; when reacted with formaldehyde and secondary amines they give Mannich bases; and when they are oxidized the furanidine ring is decomposed with the formation of imidazole-4,5-dicarboxylic acid.

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CHEMISTRY OF SELENOPHENE

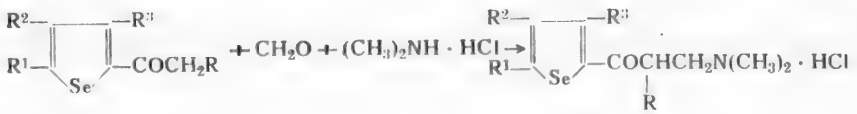
VI. AMINOMETHYLATION OF KETONES OF THE SELENOPHENE SERIES

Yu. K. Yuryev and N. K. Sadovaya

According to the literature the aminomethylation reaction – the Mannich reaction – has been successfully applied not only to ketones of the thiophene series [1-3], but also to thiophene itself, with involvement of the labile hydrogen atoms in the α-position [4]. This reaction has as yet not been applied to compounds of the selenophene series, and for this reason we thought it of interest to study the behavior of the simpler ketones of the selenophene series in the Mannich reaction.

In the present study, a continuation of our investigations on the chemistry of selenophene [5], we accomplished the aminomethylation of the following ketones of the selenophene series: methyl 2-selenienyl ketone , ethyl 2-selenienyl ketone, methyl 3-methyl-2-selenienyl ketone, ethyl 3-methyl-2-selenienyl ketone, methyl 2,4-dimethyl-5-selenienyl ketone and methyl 3,4-dimethyl-2-selenienyl ketone.

The indicated ketones were reacted with paraform and dimethylamine hydrochloride. All of the β-dimethylaminoalkyl alkyl-2-selenienyl ketone hydrochlorides obtained by this reaction were white crystalline substances, extremely stable in the air, readily soluble in water and alcohol, and insoluble in ether.



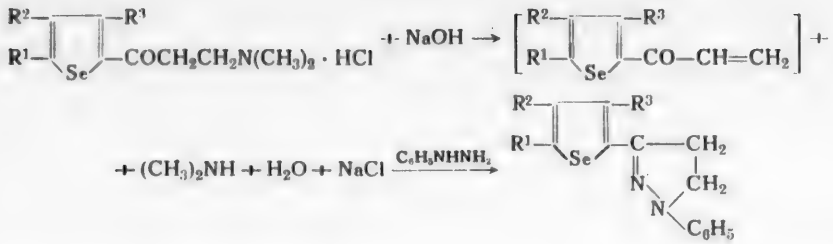
R=H, CH_3;
$R^1 = R^2 = R^3 = H$;
$R^1 = R^2 = H$ $R^3 = CH_3$;
$R^2 = H$; $R^1 = R^3 = CH_3$;
$R^1 = H$; $R^2 = R^3 = CH_3$

The β-dimethylaminoalkyl 2-selenienyl ketone hydrochlorides obtained in this manner were reacted with phenylhydrazine in order to obtain the corresponding 1-phenyl-3-(2-selenienyl)-pyrazolines.

In the thiophene series the 1-phenyl-3-(2-thienyl)-pyrazolines were usually obtained by the reaction of phenylhydrazine with vinyl 2-thienyl ketones, in turn obtained by the steam-distillation of the corresponding amino ketone hydrochlorides [3].

In the present study we accomplished the closure of the pyrazoline ring, containing the selenophene ring in the 3 position, in one reaction by reacting phenylhydrazine directly with the not isolated deamination products, namely vinyl alkly-2-selenienyl ketones, obtained in the boiling of the β-dimethylaminoalkyl alkyl-2-selenienyl ketone hydrochlorides with concentrated sodium hydroxide solution. (See the following page for diagram).

This method of closing the pyrazoline ring, omitting the separate stage of preparing and isolating the vinyl ketones, was described by A. N. Kost and V. V. Ershov [6] for the hydrochlorides of aromatic β-dialkylamino ketones.



The 1-phenyl-3-(alkyl-2-selenienyl)-pyrazolines described in the present study were obtained as yellow-orange crystalline compounds, stable in the air; their ether solutions exhibit a sky-blue fluorescence.

EXPERIMENTAL

I. Aminomethylation of Ketones of the Selenophene Series

The amino ketones of the selenophene series were synthesized as the hydrochlorides by a method similar to that described for the aminomethylation of the corresponding analogs in the thiophene series [3]. A mixture of the ketone, dimethylamine hydrochloride, paraform and anhydrous alcohol was boiled for 2-4 hours, diluted with an equal volume of water, acidified with 1-2 drops of concentrated hydrochloric acid, and extracted with ether to remove unreacted ketone. The water solution was made alkaline, and the separated amino ketone was extracted with ether; the ether solution of the amino ketone was dried over anhydrous magnesium sulfate and then saturated with dry hydrogen chloride, which resulted in the deposition of the amino ketone hydrochloride as a white precipitate. The amino ketone hydrochlorides obtained in this manner were then purified twice by dissolving in alcohol, followed by precipitation with absolute ether.

β-Dimethylaminoethyl 2-selenienyl ketone hydrochloride. From 1.6 g (0.009 mole) of methyl 2-selenienyl ketone, 1 g (0.012 mole) of dimethylamine hydrochloride, 0.4 g of paraform and 1 ml of anhydrous alcohol we obtained 1.3 g (54%) of β-dimethylaminoethyl 2-selenienyl ketone hydrochloride with m. p. 168-169°.

Found %: C 40.60, 40.68; H 4.89, 5.04; N 5.54, 5.58. $C_9H_{14}ONClSe$. Calculated %: C 40.55; H 5.29; N 5.25.

β-Dimethylaminoisopropyl 2-selenienyl ketone hydrochloride. From 0.9 g (0.005 mole) of ethyl 2-selenienyl ketone, 0.5 g (0.006 mole) of dimethylamine hydrochloride, 0.2 g of paraform and 1 ml of anhydrous alcohol we obtained 0.8 g (57%) of β-dimethylaminoisopropyl 2-selenienyl ketone hydrochloride with m. p. 150°.

Found %: C 42.90, 42.86; H 5.86, 5.74; N 5.21, 5.33. $C_{10}H_{16}ONClSe$. Calculated %: C 42.78; H 5.75; N 4.99.

β-Dimethylaminoethyl 3-methyl-2-selenienyl ketone hydrochloride. From 0.9 g (0.005 mole) of methyl 3-methyl-2-selenienyl ketone (b. p. 119-120° at 20 mm, n_D^{20} 1.5930, d_4^{20} 1.4802),* 0.5 g (0.006 mole) of dimethylamine hydrochloride, 0.2 g of paraform and 1 ml of anhydrous alcohol we obtained 0.8 g (57%) of β-dimethylaminoethyl 3-methyl-2-selenienyl ketone with m. p. 154-155°.

Found %: C 42.95, 42.72; H 6.11, 5.97; N 4.90, 5.00. $C_{10}H_{16}ONClSe$. Calculated %: C 42.78; H 5.75; N 4.99.

β-Dimethylaminoisopropyl 3-methyl-2-selenienyl ketone hydrochloride. From 1 g (0.005 mole) of ethyl 3-methyl-2-selenienyl ketone (m. p. 38-39),** 0.5 g (0.006 mole) of dimethylamine hydrochloride, 0.2 g of paraform and 1 ml of anhydrous alcohol we obtained 0.75 g (50%) of β-dimethylaminoisopropyl 3-methyl-2-selenienyl ketone hydrochloride with m. p. 138-139°.

* Methyl 3-methyl-2-selenienyl ketone is not reported in the literature and was obtained in the present study.

** Ethyl 3-methyl-2-selenienyl ketone is not reported in the literature and was obtained in the present study.

Found %: C 44.66, 44.81; H 6.21, 6.14; N 4.40, 4.50. $C_{11}H_{18}ONClSe$. Calculated %: C 44.83; H 6.15; N 4.75.

β-Dimethylaminoethyl 2,4-dimethyl-5-selenienyl ketone hydrochloride. From 2.5 g (0.012 mole) of methyl 2,4-dimethyl-5-selenienyl ketone (b. p. 121.5-122° at 10 mm; n_D^{20} 1.5849; d_4^{20} 1.4042),* 1.25 g (0.015 mole) of dimethylamine hydrochloride, 0.5 g of paraform and 2 ml of anhydrous alcohol we obtained 1.6 g (45%) of β-dimethylaminoethyl 2,4-dimethyl-5-selenienyl ketone hydrochloride with m. p. 151-152°.

Found %: C 44.72, 44.64; H 6.45, 6.57; N 4.87, 4.94. $C_{11}H_{18}ONClSe$. Calculated %: C 44.83; H 6.15; N 4.75.

β-Dimethylaminoethyl 3,4-dimethyl-2-selenienyl ketone hydrochloride. From 1 g (0.005 mole) of methyl 3,4-dimethyl-2-selenienyl ketone, 0.5 g (0.006 mole) of dimethylamine hydrochloride, 0.2 g of paraform and 1 ml of anhydrous alcohol we obtained 0.75 g (50%) of β-dimethylaminoethyl 3,4-dimethyl-2-selenienyl ketone with m. p. 153°.

Found %: C 44.68, 44.82; H 6.41, 6.49; N 4.60, 4.54. $C_{11}H_{18}ONClSe$. Calculated %: C 44.83; H 6.15; N 4.75.

II. 1-Phenyl-3-(alkyl-2-selenienyl)-pyrazolines

A solution of the amino ketone hydrochloride in methyl alcohol was added in 5-10 minutes to a mixture of 40% sodium hydroxide solution and phenylhydrazine in methyl alcohol. The mixture was boiled on the water bath for 1 hour; on cooling to room temperature the pyrazolines deposited as needle crystals with either a yellow or orange color, and were purified by recrystallization from methyl alcohol.

1-Phenyl-3-(2-selenienyl)-pyrazoline. From 2 g (0.007 mole) of β-dimethylaminoethyl 2-selenienyl ketone hydrochloride in 20 ml of methyl alcohol, 3.8 g (0.035 mole) of phenylhydrazine in 5 ml of methyl alcohol and 0.8 ml of 40% sodium hydroxide solution we obtained 1.1 g (58%) of 1-phenyl-3-(2-selenienyl)-pyrazoline. Lemon-yellow needles with m. p. 117°.

Found %: C 56.83, 56.94; H 4.22, 4.24; N 10.59, 10.41. $C_{13}H_{12}N_2Se$. Calculated %: C 56.72; H 4.40; N 10.18.

1-Phenyl-3-(3-methyl-2-selenienyl)-pyrazoline. From 0.5 g (0.002 mole) of β-dimethylaminoethyl 3-methyl-2-selenienyl ketone in 5 ml of methyl alcohol, 0.8 g (0.008 mole) of phenylhydrazine in 1 ml of methyl alcohol and 0.1 ml of 40% sodium hydroxide solution we obtained 0.28 g (50%) of 1-phenyl-3-(3-methyl-2-selenienyl)-pyrazoline. Yellow needles with m. p. 121-122°.

Found %: C 57.94, 58.17; H 4.88, 4.91; N 9.72, 9.51. $C_{14}H_{14}N_2Se$. Calculated %: C 58.13; H 4.88; N 9.69.

1-Phenyl-3-(2,4-dimethyl-5-selenienyl)-pyrazoline. From 0.2 g (0.008 mole) of β-dimethylaminoethyl 2,4-dimethyl-5-selenienyl ketone hydrochloride in 5 ml of methyl alcohol, 0.3 g (0.003 mole) of phenylhydrazine in 1 ml of methyl alcohol and 0.08 ml of 40% sodium hydroxide solution we obtained 0.1 g (42%) of 1-phenyl-3-(2,4-dimethyl-5-selenienyl)-pyrazoline. Yellow needles with m. p. 110-111°.

Found %: C 59.53, 59.39; H 5.46, 5.52; N 9.00, 9.06. $C_{15}H_{16}N_2Se$. Calculated %: C 59.39; H 5.32; N 9.24.

1-Phenyl-3-(3,4-dimethyl-2-selenienyl)-pyrazoline. From 2.3 g (0.008 mole) of β-dimethylaminoethyl 3,4-dimethyl-2-selenienyl ketone hydrochloride in 15 ml of methyl alcohol, 3.8 g (0.035 mole) of phenylhydrazine in 5 ml of methyl alcohol and 0.8 ml of 40% sodium hydroxide solution we obtained 1.3 g (54%) of 1-phenyl-3-(3,4-dimethyl-2-selenienyl)-pyrazoline. Orange-yellow needles with m. p. 123-124°.

* Methyl 2,4-dimethyl-5-selenienyl ketone is not reported in the literature and was obtained in the present study.

Found %: C 59.63, 59.73; H 5.52, 5.54; N 9.38, 9.26. $C_{15}H_{16}N_2Se$. Calculated %: C 59.39; H 5.32; N 9.24.

SUMMARY

1. The aminomethylation of ketones of the selenophene series proceeds normally, and the hydrochlorides of the corresponding amino ketones are obtained in 45-60% yields. The hydrochlorides of the following previously unknown ketones were synthesized in this manner: β-dimethylaminoethyl 2-selenienyl ketone, β-dimethylaminoisopropyl 2-selenienyl ketone, β-diemthylaminoethyl 3-methyl-2-selenienyl ketone, β-dimethylaminoisopropyl 3-methyl-2-selenienyl ketone, β-dimethylaminoethyl 2,4-dimethyl-5-selenienyl ketone and β-dimethylaminoethyl 3,4-dimethyl-2-selenienyl ketone.

2. The reaction of the hydrochlorides of the β-dimethylaminoalkyl alkyl-2-selenienyl ketones with phenylhydrazine leads to obtaining the corresponding 1-phenyl-3-(alkyl-2-selenienyl)-pyrazolines in 40-60% yields. The previously unknown 1-phenyl-3-(2-selenienyl)-pyrazoline, 1-phenyl-3-(3-methyl-2-selenienyl)-pyrazoline, 1-phenyl-3-(2,4-dimethyl-5-selenienyl)-pyrazoline and 1-phenyl-3-(3,4-dimethyl-2-selenienyl)-pyrazoline were synthesized in this manner.

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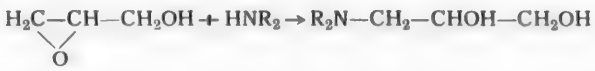
CONDENSATION OF GLYCIDOL WITH AROMATIC AMINES

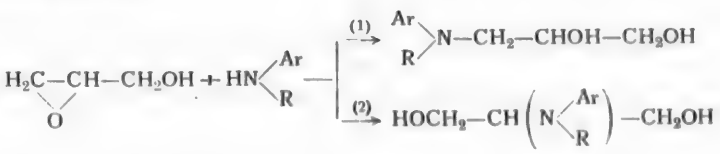
M. S. Malinovsky and V. N. Perchik

In 1930 Rider and Hill [1] investigated the condensation between glycidol and secondary amines of the aliphatic series (dimethyl-, diethyl-, dipropyl-, diisobutyl- and diisoamylamines) and also piperidine, and found that the reaction between them proceeds according to the equation

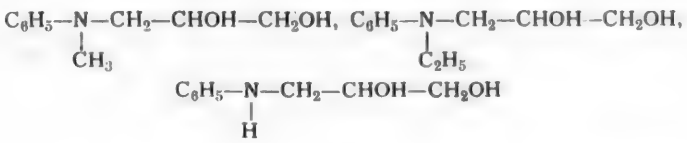


Even earlier, Knorr [2] had prepared two amino alcohols by treating dimethylamine and diethylamine with glycidol. Their structure was confirmed by synthesis from amines and glycerol monochlorohydrin. Similar products were obtained in the two cases. From this it follows that in the condensation with amines, the α-oxide ring of glycidol opened at the primary carbon atom, i.e., similar to the opening of the ring in propylene oxide treated with ammonia and amines [3].

Due to the presence of two hydroxyl groups in the α-position, the products obtained by the condensation of glycidol with amines are valuable for the synthesis of esters from acid halides and anhydrides, and thus we set ourselves the problem of synthesizing some of them, starting with aromatic amines. There are two possibilities for the direction of the reaction:



However, considering the papers mentioned above, we thought that the opening of the α-oxide ring must proceed in the first direction. To confirm this we carried out the condensation of α,α-chlorohydrin with methylaniline by Roth's method [4]. As a result we obtained a product which was identical to the one which we obtained from the same amine and glycidol. Thus the structure of the amino alcohols we synthesized are expressed by the following formulas



All the amino alcohols obtained were acetylated with acetic anhydride. The structure of the esters synthesized was confirmed by determination of the acyl groups.

$C_6H_5-N(CH_3)-CH_2-CHOCOCH_3-CH_2OCOCH_3$,

$C_6H_5-N(C_2H_5)-CH_2-CHOCOCH_3-CH_2OCOCH_3$,

$C_6H_5-N(OCOCH_3)-CH_2-CHOCOCH_3-CH_2OCOCH_3$

EXPERIMENTAL

The molar ratio of methylaniline and ethylaniline to glycidol was 1 : 1; 5 moles of aniline per mole of glycidol was used. The condensation was carried out in a round bottomed flask, fitted with a reflux condenser, a stirrer and a dropping funnel. The glycidol was gradually added to the freshly distilled amine in the flask. After 3-4 hours standing at room temperature (with stirring), the mixture was heated on a water bath with stirring for 6 hours at 60-80°. After cooling, the mixture was distilled in vacuum. A small amount of unreacted amine distilled off at first and then the amino alcohol distilled over as a thick, oily liquid, which quickly crystallized on standing. All the amino alcohols obtained were soluble in water, less so in alcohol and insoluble in ether. The amino alcohols were acylated with acetic anhydride in the usual way. After washing out the acetic acid with soda solution and water, the esters obtained were extracted with ether and dried with anhydrous sodium sulfate. After the solvent was distilled off, the esters were distilled in vacuum. The acyl groups were determined by the usual method.

1. β,γ-Dihydroxypropylmethylaniline

$C_6H_5-N(CH_3)-CH_2-CHOH-CH_2OH$

is a colorless, crystalline substance with m.p. 74-75°, b.p. 170-172° (3-4 mm). The yield was 38%.

Found %: N 7.90; C 65.15; H 8.24. $C_{10}H_{15}O_2N$. Calculated %: N 7.13; C 66.20; H 8.27.

The diacetate is a liquid with b.p. 153° (1 mm) d_4^{20} 1.100, n_D^{20} 1.5179. The yield was 70%. The amount of OH groups found corresponded to 2.

2. β, γ-Dihydroxypropylethylaniline

$C_6H_5-N(C_2H_5)-CH_2-CHOH-CH_2OH$

is a colorless, crystalline substance with m.p. 59°, b.p. 170-172° (3-4 mm).

Found %: N 7.64; C 64.37; H 8.78. $C_{11}H_{17}O_2N$. Calculated %: N 7.18; C 67.60; H 8.71.

The diacetate is a liquid with b.p. 154-155° (1 mm), d_4^{20} 1.110, n_D^{20} 1.515. The yield was 98%. After carrying out hydrolysis, we found 2 acyl groups.

3. β,γ-Dihydroxypropylaniline

$C_6H_5-NH-CH_2-CHOH-CH_2OH$

is a crystalline substance with m.p. 48-49°, b.p. 190° (4 mm).

Found %: N 8.42; C 62.84; H 7.84. $C_9H_{13}O_2N$. Calculated %: N 8.38; C 64.67; H 7.79.

The diacetic ester is a liquid with b.p. 167° (1.5 mm), d_4^{20} 1.160, N_D^{20} 1.5120. The yield was 60%. On hydrolyzing, we found 3 acyl groups.

SUMMARY

Methylaniline, ethylaniline and aniline condensed with glycidol to give amino alcohols of the general formula $Ar-N(R)-CH_2CHOH-CH_2OH$. Amino alcohols of this structure were readily acetylated with acetic anhydride, giving the corresponding esters.

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* In Russian.

INVESTIGATIONS IN THE FIELD OF ALKOXYSILANES

VIII. ALKYL(ARYL)ACETOXYSILANES AND THEIR REACTIONS WITH ALIPHATIC ALCOHOLS*

B. N. Dolgov, V. P. Davydova and M. G. Voronkov

Comparatively recently the alkylacetoxysilanes $RSi(OCOCH_3)_3$ and $R_2Si(OCOCH_3)_2$ have attracted the attention of many investigators as suitable materials for rendering substances of organic origin hydrophobic [2-12]. In contrast to the corresponding alkylchlorosilanes $RSiCl_3$ and R_2SiCl_2, which had previously been proposed for this purpose, the use of alkylacetoxysilanes results in the liberation not of agressive hydrogen chloride, but of acetic acid, which does not destroy the acid-sensitive materials being treated (for example cellulose).

In a comparative investigation of the properties of various water repellent organosilicon coatings,** we found the study of the hydrophobic effect of alkylacetoxysilanes interesting. We decided to investigate the relation of this effect to the structure of the radical and the number of acetoxy groups in $R_nSi(OCOCH_3)_{4-n}$ ($n = 1-3$), as well as the mechanism of hydrophobization of organic hydroxyl-containing materials (mainly cellulose) and for this it was first necessary to investigate the reaction of alkylacetoxysilanes with the simplest organic compounds of this type, namely, alcohols. The present paper is devoted to this problem.

The simplest and most convenient methods of synthesizing alkylacetoxysilanes are based on the reaction of appropriate alkylchlorosilanes with acetic anhydride [6, 7, 12, 14-16], salts of acetic acid [2-5] and, finally, with acetic acid itself, in the presence of its salts, acetic anhydride [4, 8, 11] or tertiary amines [17].***

The comparative investigation of these methods we carried out showed that the best of them in simplicity of procedure and also in yields, is the method based on the reaction of alkylchlorosilanes with acetic anhydride. Using this method, we synthesized 7 alkyl(aryl)triacetoxysilanes $RSi(OCOCH_3)_3$, where R = CH_3, C_2H_5, n-C_2H_9, sec-C_4H_9, iso-C_4H_9, cyclo-C_6H_{11} and C_6H_5 and 2 dialkyldiacetoxysilanes $R_2Si(OCOCH_3)_2$, where R = CH_3, C_2H_5. Four compounds (R = n-C_4H_9, sec-C_4H_9, iso-C_4H_9 and cyclo-C_6H_{11}) were previously unknown. Phenyltriacetoxysilane [16] also had not been obtained in a pure state. The physical properties, yields and analysis data of the alkylacetoxysilanes we synthesized are given in Table 1.

We also prepared dimethyldiacetoxysilane by circulating the vapor of dimethyldichlorosilane (dissolved in benzene) over sodium acetate. This made it possible to increase the yield to 76% as compared with the 50% yield reported in the literature [3].

The reaction of acetoxysilanes with alcohols may proceed either by scheme (1) [1, 15]

$$\equiv Si{-}OCOCH_3 + ROH \rightarrow \equiv Si{-}OR + CH_3COOH, \quad (1)$$

or by scheme (2) [1, 19]

$$\equiv Si{-}OCOCH_3 + ROH \rightarrow \equiv Si{-}OH + CH_3COOR \quad (2)$$

* For preceding report see [1].

** For a review of papers in this field see [13].

*** See also [18] for the literature on this problem.

TABLE 1

The Physical Properties, Analysis Data and Yields of Alkyl(aryl)acetoxysilanes

Formula	Boiling point	Pressure (in mm)	d_4^{20}	n_D^{20}	MR_D		Ester number		Si content (%)		Yield (%)
					calc.	found	calc.	found	calc.	found	
$CH_3Si(OCOCH_3)_3$	87—88° (m.p. 40.3°)	3	—	—		—	—	—	12.75	12.80, 12.89 **	70
$(CH_3)_2Si(OCOCH_3)_2$	165	750	1.0540	1.4030	41.06	40.8	453.8	455.8, 457.9	—	—	94
$(CH_3)_3SiOCOCH_3$	103—104	760	0.8914	1.3875	35.37	34.96	424.2	426.1, 425.7	—	—	35
$C_2H_5Si(OCOCH_3)_3$	107.5—108.5	8	1.1428	1.4123	51.08	51.04	512.2	508.2, 511.7	—	—	70
$(C_2H_5)_2Si(OCOCH_3)_2$	73.3	5	1.0240	1.4152	50.32	49.98	420.5	410.2, 415.7	—	—	90
$n\text{-}C_4H_9Si(OCOCH_3)_3$	112—114	4	1.0872	1.4155	60.34	60.48	457.4	442.2, 438.4	10.70	10.61, 10.57	74.5
$iso\text{-}C_4H_9Si(OCOCH_3)_3$	101—102	4	1.0964	1.4158	60.34	60.02	457.4	453.8, 459.5	10.70	10.54, 10.58	78
$sec\text{-}C_4H_9Si(OCOCH_3)_3$	116—117	7	1.0988	1.4185	60.34	60.22	457.4	453.4, 454.7	10.70	10.92, 10.89	81
$cyclo\text{-}C_6H_{11}Si(OCOCH_3)_3$	121—122	2	1.1367	1.4430	67.47	67.25	416.2	413.6, 414.3	9.74	9.89, 10.05	70
$C_6H_5Si(OCOCH_3)_3$	153 (m.p. 34.5°)	1	1.1939	1.4708	66.27	66.07	—	—	9.90	9.98, 10.08***	35.5

* According to Warrick [25].

** Calculated %: C 38.16; H 5.49. Found %: C 38.15, 37.94; H 5.55, 5.54.

*** Calculated %: C 51.1; H 5.00. Found %: C 51.29; H 4.99, 5.09.

TABLE 2

Amount of $CH_3Si(OCOCH_3)_3$ (II) (in g)	Amount of tert-C_4H_9OH (II) (in g)	Molar ratio (I : II)	Duration of synthesis (in hours)	Yield of $CH_3(tert\text{-}C_4H_{90})_2SiOCOCH_3$ (in g)	Yield of $CH_3(tert\text{-}C_4H_{90})_2SiOCOCH_3$ (in %)	Remarks
52.2	35.1	1 : 2	3	34.7	59	All the mixture was distilled at atmospheric pressure.
51.8	61	1 : 3.5	3.5	37	63.3	
54.5	91.6	1 : 5	8	56.7	56.7	
65.5	77.1	1 : 3.5	28	42.5	57.6	After distilling off acetic acid, distilled in vacuum (11 mm).
53.7	53.8	1 : 3	10	46.2	76.3	After distilling off acetic acid, distilled in vacuum (3 mm).

If the acetic acid is distilled off at atmospheric pressure, the alkyltriacetoxysilanes react with alcohols according to Scheme (2), like silicoacetic anhydride [1]. At lower temperatures, which may readily be attained by distilling off the acetic acid formed by Scheme (1) in vacuum, one, two or all three acetoxy groups in $RSi(OCOCH_3)_3$ may be changed for alkoxy groups.*

In the case of tertiary alcohols (tert-C_4H_9OH), under the given conditions only two acetoxy groups are exchanged for the tert-alkoxy group in alkyl- and arylacetoxysilanes [$CH_3Si(OCOCH_3)_3$ and $C_6H_5Si(OCOCH_3)_3$] and only one acetoxy group in dialkyldiacetoxysilanes [$(CH_3)_2Si(OCOCH_3)_2$].

As tertiary alcohols undergo acetylation with more difficulty than primary and secondary ones, the products of their reaction with alkyl(aryl)acetoxysilanes could be distilled at normal pressure. However, in this case also, prolonged heating of the reaction mixture lead to a decrease in the yields of tert-alkoxyacetoxy derivatives, regardless of the amount of excess alcohol used (Table 2).

The data we obtained showed that the reaction between alkyl(aryl)acetoxysilanes $R_nSi(OCOCH_3)_{4-n}$ (R = alkyl, aryl; n = 1-2) with alcohols R'OH, which proceeded rapidly and did not require much heating, was a very simple and convenient method of synthesizing alkyl(aryl)alkoxysilanes $R_nSi(OR')_{4-n}$ and alkyl(aryl)-alkoxyacetosilanes

$$R_nSi(OR')_m(OCOCH_3)_{4n-m}\ (n = 1,\ m = 1.2 \text{ and } n = 2,\ m = 1).$$

Tables 3 and 4 give the physical properties, yields and analysis data of 15 organosilicon compounds, of the classes mentioned above, which we synthesized by this method (10 of them, given in Table 4, were previously unknown).

EXPERIMENTAL

Starting materials. The acetic anhydride (commercial, chemical pure preparation) was distilled before adding to the reaction. The starting alcohols were purified by two distillations over metallic calcium. The alkylchlorosilanes (products of direct synthesis or the addition of $HSiCl_3$ to the appropriate olefins) were purified by distillation on an efficient column.

Method of Performing Syntheses

Synthesis of alkyl(aryl)acetoxysi lanes. Alkyl(aryl)chlorosilanes were mixed with excess acetic anhydride in a flask with a pear fractionating column. Over 18-20 hours, close to the theoretical amount of acetyl chloride (b.p. 50-52°) was slowly distilled off from the reaction mixture and the reaction product was isolated by fractional distillation in vacuum.

* The yield of the trialkoxy derivative was low in the case of sec-octyl alcohol.

TABLE 3

Physical Properties, Analysis Data and Yields of Alkyl(aryl)alkoxysilanes

$RSi(OR')_3$	Boiling point	Pressure (mm)	d_4^{20}	n_D^{20}	MR_D		Content (in %)						Yield (in %)
							Si		C		H		
					calc	found	calc	found	calc	found	calc	found	
$CH_3Si(OC_3H_7)_3$	83.5°	13	0.8831	1.3990	60.34	60.36	12.74	12.67, 12.79	54.49	54.42, 54.33	10.97	10.91, 10.99	79
$CH_3Si[OCHCH_2(CH_3)_2]_3$	101.5	18	0.8690	1.4048	74.23	73.99	10.70	10.69, 10.49	59.48	59.19, 59.29	11.52	11.42, 11.35	47
$CH_3Si[OCHCH_3(C_6H_{13})]_3$	201—202	2	0.8607	1.4310	129.79	129.55	6.52	6.73, 6.69	69.7	69.87, 69.75	12.64	12.68, 12.75	24
$C_2H_5Si(OC_4H_9)_3$	128	12	0.8787	1.4145	78.86	78.71	10.15	10.05, 10.24	60.82	60.77, 60.44	11.43	11.76, 11.85	84
$C_6H_5Si(OC_4H_9)_3$	165—167	7	0.9450	1.4608	94.05	94.20	8.65	8.52, 8.58	66.61	66.18, 66.38	9.93	9.88, 9.80	42

* According to Warrick [25].

TABLE 4

Physical Properties, Analysis Data and Yields of Alkyl(aryl)alkoxyacetoxysilanes

Formula of substance	Boiling point	Pressure (mm)	d_4^{20}	n_D^{20}	Molecular weight		Si content (in %)		Ester number		Yield (in %)
							calc	found	calc	found	
CH_3(tert-$C_4H_9O)_2SiOCOCH_3$	71.5°	5	0.9431	1.4020	248.1	238.2	11.32	11.21, 11.43	226.1	232.9, 233.1	76
CH_3(tert-$C_4H_9O)Si(OCOCH_3)_2$	91	10	1.0320	1.4045	234.3	—	11.98	11.87, 11.83	341.1	339.3, 340.8	66
$(CH_3)_2$(tert-$C_4H_9O)SiOCOCH_3$	155.6	757	0.9318	1.3995	190.32	188.8	14.76	14.85, 14.79	294.7	298.2	63
C_6H_5(tert-$C_4H_9O)_2SiOCOCH_3$	137—139	8	1.0044	1.4611	310.46	—	9.04	8.87, 8.76	180.7	179.5, 177.1	64
CH_3(tert-$C_5H_{11}O)_2SiOCOCH_3$	92—94	1	0.9221	1.4130	276.5	274.5	10.16	10.15, 10.29*	—	—	52
CH_3(iso-$C_5H_{11}O)_2SiOCOCH_3$	118—119	9	0.9273	1.4131	276.5	—	10.16	10.26, 10.29	202.9	204.2, 205.5	40
CH_3(iso-$C_5H_{11}O)Si(OCOCH_3)_2$	108—109	11	1.0333	1.4085	248.35	—	11.31	11.56, 11.65	326.2	325.6, 324.7	85
CH_3(sec-$C_8H_{17}O)_2SiOCOCH_3$	150—151	1	0.9151	1.4250	360.6	359.7	7.79	8.25, 8.28	155.5	150.1, 153.2	20
CH_3(sec-$C_8H_{17}O)Si(OCOCH_3)_2$	115—116	1	0.9879	1.4170	290.43	295.8	9.67	9.72, 9.77	275.6	270.5, 273.4	40
$(CH_3)_2$(sec-$C_4H_9O)SiOCOCH_3$	44.5—46	3	0.9203	1.4021	190.32	—	14.76	14.31, 14.15	294.7	297.6 —	77

* Calculated %: C 56.48; H 10.21. Found %: C 56.36, 56.58; H 10.19, 10.29.

Reaction of alkyl(aryl)acetoxysilanes with alcohols. The syntheses were carried out in a three-necked round-bottomed flask, fitted with a stirrer with a mercury seal, a dropping funnel, a thermometer and a reflux condenser, closed with a calcium chloride tube. The alkyl(aryl)acetoxysilane was placed in the flask and with stirring, sufficient alcohol added dropwise to substitute one, two or three acetoxy groups.

On mixing, the temperature rose to 60-70° in the case of primary and secondary alcohols. The reaction mixture was stirred for 1-2 hours and then fractionally distilled in vacuum. The reaction products were purified by a second distillation. The use of excess alcohol and boiling and mixture lowered the yield of product obtained. In the case of tertiary butyl alcohol, the reaction mixture was heated to 130-140° with stirring, when the acetic acid distilled off at atmospheric pressure and the reaction product was isolated by fractional distillation in vacuum or at atmospheric pressure.

Analysis. The silicon, carbon and hydrogen contents of the alkyl(aryl)trialkoxysilanes were determined on one sample combusted with a stream of oxygen. The silicon contents of the other substances were determined by mineralization of a sample of the substance with a mixture of nitric acid and oleum (1 : 3). The ester numbers of the substances with two and three acetoxy groups were determined by titrating a sample of the substance, dissolved in a mixture of equal parts of acetone and water, with 0.2 N NaOH solution [20]. The ester numbers of substances containing one acetoxy group were determined by heating a sample of the substance with a 0.5 N solution of KOH in diethylene glycol and subsequently titrating the excess alkali with 0.5 N HCl [21]. The most characteristic experiments are described below.

Synthesis of phenyltriacetoxysilane. 163.5 g of phenyltrichlorosilane and 260.2 g of acetic anhydride were mixed in a flask with a pear fractionating column. After distilling off the acetyl chloride, a fractional distillation in vacuum gave 79 g (35.5%) of phenyltriacetoxysilane with b.p. 153° (1 mm), d_4^{20} 1.1939, n_D^{20} 1.4708 (for a supercooled melt). On cooling to −8°, the phenyltriacetoxysilane slowly crystallized, forming white, needle-like crystals with m.p. 34.5°. The residue after distillation was a brown, viscous tar, which, in the molten state, could be pulled out into very fine threads, which, however, quickly lost their plasticity on standing in air.

Synthesis of dimethyldiacetoxysilane by a reaction in the vapor phase. 30 g of anhydrous sodium acetate was mixed with glass dispersers and placed in a Soxhlet extractor. A solution of 30 g of dimethyldichlorosilane in 70 ml of dry benzene was heated to boiling in the flask of the extractor. The vapor of the dimethyldichlorosilane and benzene interacted with the sodium acetate for 3 hours. Then the mixture of salts was extracted twice with pure benzene. After distilling off the benzene, the solution in the flask of the extractor yielded 20 g (76%) of dimethyldiacetoxysilane with b.p. 165° (750 mm), d_4^{20} 1.0540, n_D^{20} 1.4030.

Dimethyldiacetoxysilane was also prepared by reacting dimethyl dichlorosilane with acetic anhydride; the yield was 90%.

Reaction of methyltriacetoxysilane with n-propyl alcohol. 23.5 g of n-propyl alcohol was added with stirring to 28.5 g of methyltriacetoxysilane. The temperature of the mixture rose to 70°. The mixture was stirred for 1 hour, while cooled in ice water, then it was fractionally distilled in vacuum. We obtained 22.8 g (79%) of methyltri-n-propoxysilane with b.p. 85.5-86.5° (14 mm), which after a second distillation had b.p. 83.5° (13 mm), d_4^{20} 0.8831, n_D^{20} 1.3990. Literature data [22] b.p. 90-91° (20 mm), d_4^{25} 0.8789, n_D^{25} 1.3970.

Reaction of methyltriacetoxysilane with tert-butyl alcohol. Methyl triacetoxysilane and tert-butyl alcohol were mixed in various molar ratios (from 1 : 2 to 1 : 5, see Table 2). The temperature of the mixtures rose to 40°. The mixture was then heated to 120-130° for 3-28 hours. In all cases fractionation in vacuum gave various yields (Table 2) of methyl-di-tert-butoxyacetoxysilane with b.p. 195-197°, which had the constants given in Table 4 after a second distillation.

On slowly adding 26.4 g of tert-butyl alcohol to 78.5 g of methyltriacetoxysilane and mixing for 1 hour, followed by distillation in vacuum, we obtained 55 g of methyl-tert-butoxydiacetoxysilane with b.p. 88-90° (9 mm), which had the properties given in Table 4 after a second distillation. In addition, we obtained 11.5 g (12.5%) of methyl-di-tert-butoxyacetoxysilane with b.p. 90-92° (9 mm), n_D^{20} 1.4025.

Reaction of ethyltriacetoxysilane with n-butyl alcohol. a) 31.5 g of n-butyl alcohol was added to 27.5 g of ethyltriacetoxysilane. The temperature of the mixture rose to 57°. After 12 hours the mixture was distilled at atmospheric pressure. 44 g (99%) of butyl acetate distilled off in the range 117-121°. The residue was a viscous tar.

In a similar reaction between ethyltriacetoxysilane and methyl alcohol, we also obtained the theoretical amount of methyl acetate and gelatinous polymer. b) 41.5 g of n-butyl alcohol was added to 37.5 g of ethyltriacetoxysilane. The mixture was cooled in ice water. After 2 hours stirring, it was fractionated in vacuum, to give 37.5 g of ethyl-tri-n-butoxysilane, b.p. 123-126° (11 mm). The yield was 84%. After a second distillation, we obtained a substance, which had the constants given in Table 3. Literature data [23]: b.p. 235-238°, d_4^{20} 0.878, n_D^{24} 1.4128.

Reaction of phenyltriacetoxysilane with n-butyl alcohol. 27 g of phenyltriacetoxysilane was mixed with 25 g of n-butyl alcohol. The temperature of the mixture rose to 57°. After stirring and heating to 100-120° for 1 hour, the reaction mixture was fractionated in vacuum. The yield of phenyltributoxysilane with b.p. 163-168° (6 mm) was 16 g (42%). For the constants after a second distillation see Table 3.

Literature data [24]: b.p. 115-116° (0.2 mm), d_4^{20} 0.9447, n_D^{20} 1.4610.

SUMMARY

8 Alkylacetoxysilanes, phenyltriacetoxysilane and cyclohexyltriacetoxysilane were synthesized by reacting the appropriate organochlorosilanes with acetic anhydride (of these compounds, 4 were previously unknown). We investigated the reaction of alkyl(aryl)acetoxysilanes with alcohols and by this means synthesized 5 alkyl-(aryl)trialkoxysilanes and 10 alkyl(aryl)acetoxyalkoxysilanes (10 of them for the first time).

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HIGH MOLECULAR WEIGHT COMPOUNDS

C. THE RELATION OF THE SOFTENING POINT OF POLYAMIDES AND POLYESTERS TO THE STRUCTURE OF THE UNITS

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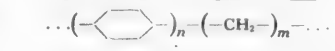
As the melting point is the simplest constant to determine and is known for all the linear polyesters and polyamides, one may use it to obtain a fairly good idea of the magnitude of the forces binding polyamide and polyester macromolecules and the relation of these forces to the structure of the elementary links of the chains.

The basic skeletal structures, present in these classes of polymers, are given in Table 1.

TABLE 1

Sample number	Skeletal structure	
	Name	Formula
1	Polymethylene	...$-CH_2-CH_2-CH_2-CH_2-CH_2-$...
2	Polyphenylene	
3	Combination of polymethylenes and polyphenylenes in various arrangements	
4	Hydrogenated polyphenylene	
5	Combination of hydrogenated polyphenylene with polymethylene	

The ester bond, typical of heterochain polyesters, and the amide bond, typical of heterochain polyamides, are groups which are present in the main macromolecular chain and dilute the basic structures given.

In addition, the macromolecular chains may contain an ether bond or sulfide and sulfonate bonds, as well as various side groups, which affect the polymer properties.

Figure 1 shows how the melting points of ethylene glycol polyesters change depending on the number of carbon atoms in the polymethylenedicarboxylic acid. Figure 2 shows the same relation for eicosamethylene glycol. As Figs. 1 and 2 show, there is a definite relation between the melting points of polyesters and the number of carbon atoms in the dicarboxylic acid [1-5].

A characteristic of these curves is the sharp difference between the melting points of the polyesters of even and odd dicarboxylic acids. As a result of this, the melting-point curves of the homologous series have a zig-zag form, as other investigators have also noted. This phenomenon, which we have defined as the "evenness factor," apparently may be explained by polar influences in dicarboxylic acid and glycol molecules. The effect of the evenness factor decreases with an increase in the number of methylene groups in the dicarboxylic acid molecule.

It should be noted that the data we obtained [1, 2] do not confirm the conclusion of Hill and Walker [6] that the melting point of a polyester is determined by the total number of methylene groups in the polyester

Fig. 1. Changes in melting points of ethylene glycol polyesters.

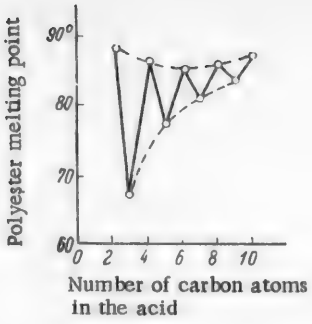


Fig. 2. Changes in melting point of eicosamethylene glycol polyesters.

chain and does not depend on the distribution of these groups, i.e., whether they are in the acid or the glycol molecule. Actually, the melting point of a polyester depends not only on the total number of methylene groups in the polyester chain, but also on their distribution between acid and glycol residues.

Figure 3 shows the changes in melting point of dicarboxylic acid polyesters in relation to the number of carbon atoms in the starting glycols [4-6], which have an even number of methylene groups in the molecule. It can be seen from Fig. 3 that the melting points of polyesters of oxalic, malonic and succinic acids change along curves that have minima corresponding to the polyester of these acids with hexamethylene glycol.

On examination of the curves of melting-point changes of triethylene glycol and propylene glycol polyesters, shown in Figs. 4, and 5, it is apparent that they differ from the curves of polymethylene glycols [4]. This difference lies in the fact that the melting points of these polyesters are much lower than those of the corresponding methylene glycol polyesters. Furthermore, the effect of the evenness factor shows up much less here and is equal to zero for propylene glycol polyesters.

TABLE 2

Softening Points of Polyesters of Dicarboxylic Acids and Glycols

Glycol	Acids											
	Diglycolic	Glutaric	β-methyl-adipic	Adipic	Thiodivaleric	Sulfonyl-divaleric	Terephthalic	Isophthalic	Phthalic	p,p'-diphenyl-dicarboxylic	m,m'-diphenyldicarboxylic	Diphenic
Ethyl glycol	17	—19	—31	47	25	82	256	103	63	330	119	96
Trimethylene glycol	29	35	—35	36	—	—	217	92	—	246	76	70
Tetramethylene glycol	67	36	—43	57	37	86	222	88	17	255	62	34
Pentamethylene glycol	30	22	—45	36	40	84	134	76	6	160	57	8
Hexamethylene glycol	47	28	—47	55	47	90	148	75	0	195	52	4
Decamethylene glycol	61	55	— 3	70	54	98	127	34	—27	126	86	— 7
Eicosamethylene glycol	86	77	57	85	76	114	108	47	47	112	89	—18
Diethylene glycol	2	—30	—29	—29	—39	64	65	55	10	117	69	54
Triethylene glycol	—6	—36	—42	—39	—41	32	60	60	— 8	86	43	38
Propylene glycol	17	—25	—25	—25	—39	65	106	80	45	130	93	39
Butanediol-1,3	1	—36	—34	—36	—42	24	82	50	— 8	125	85	36

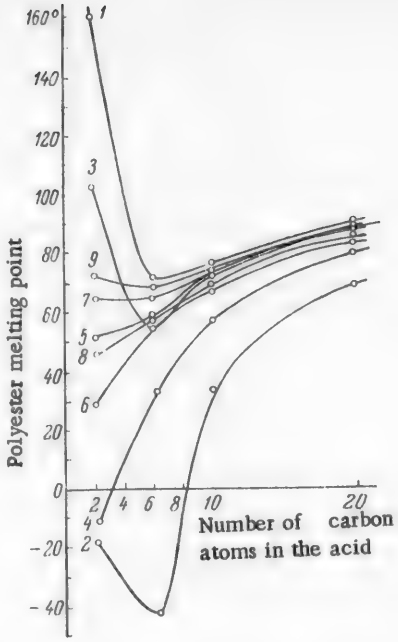


Fig. 3. Changes in melting point of dicarboxylic acid polyesters in relation to the number of carbon atoms in the glycol.
Acids: 1) oxalic, 2) malonic, 3) succinic, 4) glutaric, 5) adipic, 6) pimelic, 7) suberic, 8) azelaic, 9) sebacic.

To understand the reasons for the differences in polyester melting points, one should take into account the fact that there are three different types of groups (methylene, carbonyl and ether) in the make-up of a polyester macromolecule, which affect the melting points of the compounds containing these groups in different ways.

Almost all aliphatic polyesters (with the exception of polyethylene oxalate whose melting point is 159°) melt at lower temperatures than polymethylene (m.p. 132°). Apparently, this decrease in the melting point of a polyester in comparison with that of polymethylene is due to increased flexibility of the polymer chain, observed on introducing an oxygen link into it. The increase in flexibility of chains, containing oxygen links, is due to the fact that the rotation of methylene groups around the bond connecting them, is not completely free due to the interaction of hydrogen atoms when they approach each other at the turn. An activation energy of up to 3000 cal/mole [7] is required to overcome this interaction. In the case of the C–O-bond the activation energy is practically equal to zero, as there are not substituents on the oxygen atom to hinder free rotation around the C–O bond. For this reason the presence of C–O–C bonds in a chain increases its flexibility. This explanation is justifiable not only for polymers, but also for compounds of low molecular weight, as can be seen from the curves in Fig. 6, which show the changes in melting point in homologous series of paraffinic hydrocarbons, ethers, ketones and esters of carboxylic acids [2].

Consequently, in aliphatic polyesters there are two factors, counteracting each other and controlling the melting point of the polymer: on the one hand, the oxygen link which lowers it (in comparison with polymethylene), and on the other hand, the carbonyl group which, on the contrary, increases the melting point due to the appearance of a clearly expressed polarity and an increase in the chain rigidity. In addition, one should add the effect of the evenness factor which appears in going from the series of even dicarboxylic acid polyesters to the series of odd dicarboxylic acid polyesters. The evenness factor has not yet been fully explained [2]. Its effect may possibly be understood when the polar influences in a dicarboxylic acid molecule are considered. The effect of the evenness factor is weakened by the introduction of ether links and is reduced to zero by the introduction of a side methyl group, as is convincingly shown by propylene glycol and β-methyladipic acid polyesters (Table 2).

Although, in general, the effect of an ether-oxygen link and a side methyl group are equal in that both induce a decrease in the crystallinity of a polymer, however, their relative effectiveness is different. If their effectiveness in eliminating the effect of the evenness factor is compared, then one can say that the effect of the side methyl group is equal, in our case, to the effect of three ether links, i.e., one side methyl group is approximately 3 times more effective than one ether link as a factor disrupting the crystallinity of the polymer.

The accumulation of a large number of methylene groups in a polyester molecule, results, as a rule, in an increase in melting point if it is less than the melting point of polymethylene (i.e., lower than 132°). Polyesters of ethylene glycol with oxalic acid have melting points higher than this, which do not depend on the methylene groups, but are determined by the presence of a large number of carbonyl groups.

There is a noticeable increase in melting point as a result of the accumulation of a large number of methylene groups in the molecule, which occurs earlier in individual cases and invariably, as a rule, in

TABLE 3

Melting Points, Found and Calculated for Polyamides with Even Numbers of Methylene Groups in the Chain [8]

Name	Formula	Amine group content (in mole %)	Melting point	
			found	calc.
Polytetramethylene adipamide	$-NH(CH_2)_4NHCO(CH_2)_4CO-$ . . .	25.00	280°	282°
Polyhexamethylene adipamide	$-NH(CH_2)_6NHCO(CH_2)_4CO-$ . . .	20.00	250	250
Polytetramethylene suberamide	$-NH(CH_2)_4NHCO(CH_2)_6CO-$ . . .	20.00	250	250
Polytetramethylene sebacamide	$-NH(CH_2)_4NHCO(CH_2)_8CO-$ . . .	16.66	232	226
Poly-7-enanthoamide	$-NH(CH_2)_6CO-$	16.66	223	226
Polyoctamethylene adipamide	$-NH(CH_2)_8NHCO(CH_2)_4CO-$ . . .	16.66	235	226
Polyhexamethylene suberamide	$-NH(CH_2)_6NHCO(CH_2)_6CO-$ . . .	16.66	225	226
Polyhexamethylene sebacamide	$-NH(CH_2)_6NHCO(CH_2)_8CO-$ . . .	14.28	210	210
Polyoctametamethylene subcramide	$-NH(CH_2)_8NHCO(CH_2)_6CO-$ . . .	14.28	202	210
Poly-9-pelargonamide	$-NH(CH_2)_8CO-$	12.50	195	197
Polyoctamethylene sebacamide	$-NH(CH_2)_8NHCO(CH_2)_8CO-$ . . .	12.50	197	197
Polydecamethylene sebacamide	$-NH(CH_2)_{10}NHCO(CH_2)_8CO-$ . . .	11.11	194	187
Poly-11-undercanamide	$-NH(CH_2)_{10}CO-$	10.00	180	180
Poly-17-margaramide	$-NH(CH_2)_{16}CO-$	6.25	150	153

TABLE 4

The Number of Amide Groups Bound by Hydrogen Bonds in the AH + SH System

The ratio of starting materials (in moles) in the mixed polyamide AH + + SH	Melting point	Amount			
		hydrogen bonds (in moles %) found from the melting point	amide bonds (in mole %) calculated on the structural formula	unbound amide groups	
				(in mole %)	(in %)
1.0 + 0.0	250°	20.00	20.00	0.0	0.0
0.8 + 0.2	220	15.71	18.52	3.81	15.17
0.6 + 0.4	190	11.43	17.24	5.81	33.71
0.4 + 0.6	185	10.71	16.13	5.42	33.61
0.2 + 0.8	190	11.43	15.15	3.72	24.56
0.0 + 1.0	210	14.28	14.28	0.0	0.0

polyesters of sebacic acid. Apparently, sebacic acid represents the limit, above which the accumulation of a large number of methylene groups results in the appearance of a new character, namely – the effect of all the other groups is completely suppressed and the effect of the methylene groups becomes the determining one, and as a result the polyester acquires more and more the properties of the corresponding paraffinic compound, i.e., polymethylene.

The structure of the starting materials affects the melting points of polyamides, the same as in the case of polyesters.

We have proposed an equation which relates the melting point of polyamides to the number of hydrogen bonds [8]: $y = 7x + 110$, where y is the melting point in °C and x is the number of hydrogen bonds in molar percentage.

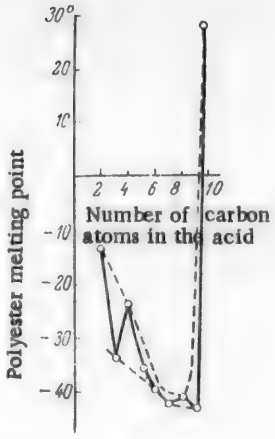


Fig. 4. Changes in melting point of triethylene glycol polyesters.

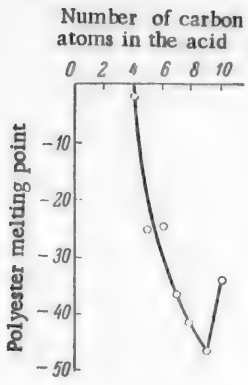


Fig. 5. Changes in melting point of propylene glycol polyesters.

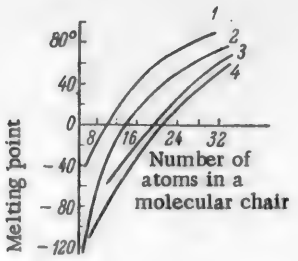


Fig. 6. Changes in melting point in relation to the number of atoms in a molecular chain. 1) Ketones $[(C_nH_{2n+1})_2CO]$, 2) paraffinic hydrocarbons (C_nH_{2n+2}), 3) esters $(C_{n-1}H_{2n-1}COOC_nH_{2n+1})$, 4) ethers $[(C_nH_{2n+1})_2O]$.

The melting points calculated by this formula and found experimentally coincide (Table 3) in the case of polyamides of dicarboxylic acids and diamines or amino acids with an even number of methylene groups in their molecules.

Here the distribution of methylene groups between the diamine and dicarboxylic acid does not matter, as can be seen from a comparison of polyhexamethylene adipamide and polytetramethylenesuberamide. Both have a 20.00% amide content and melt at 250°. Therefore, we proposed to examine polyamides as copolymers of ethylene and isocyanic acid which can be expressed in a general form by the formula $(CH_2{=}CH_2)n\cdot(CO{=}{=}NH)\,m$. The relative position of these components does not affect the melting point: if the ratio: $\frac{CO{=}NH}{CH_2{=}CH_2}=\frac{50\,m}{n}$, i.e., the molar percent of amide groups is the same, then the melting points will be equal [8].

Especially effective is the capacity of amide groups for reacting with each other to form hydrogen bonds, as a result of which a lattice of hydrogen bonds is formed between the separate macromolecules, as has been shown by Fuller, Baker and Pape [9], and also by Brill [10] and other authors [11-13].

The possibility of hydrogen bond formation is determined primarily by the stereochemistry of the macromolecules. Thus, in the case of copolymers – mixed polyamides – obtained even from even diamines and dicarboxylic acids, not all of the amide groups can form hydrogen bonds. In this case it is necessary to differentiate between the total number of amide groups and the number of amide groups bound by hydrogen bonds (number of hydrogen bonds), as they do not coincide and the first always exceeds the second.

Using the melting points of copolymers found experimentally, we calculated the number of hydrogen bonds and compared it with the number of amide groups [8, 14].

Table 4 gives these values for systems of mixed polyamides obtained from hexamethylenediammonium adipate (AH) and hexamethylenediammonium sebacinate (SH) in various ratios [8, 19].

In the case of the two salts of the dicarboxylic acids with one diamine, the minimum on the melting point curve corresponds to a product containing 60 mole% of the component with the longer chain; in the SH + + AH system this would be a product containing 60 mole% of SH. As can be seen from the data in the table, the products, containing 60% of the one or the other component, have the greatest relative loss of hydrogen bonds; furthermore, in the case of a product containing 60 mole% of the longer component, this loss is greater in absolute value as well, due to the decrease in the total number of amide groups.

TABLE 5

The Number of Amide Groups Bound by Hydrogen Bonds in Odd Polyamide Molecules [8]

Sample number	Polyamide formula	Melting point		Number		
		found experimentally	calculated on the number of amide groups	amide groups, calc on the structural formula	hydrogen bonds (in mole %)	amide groups, bound by hydrogen bonds (in %)
1	$-NH(CH_2)_5NHCO(CH_2)_5CO-$ . . .	183°	250°	20.00	10.43	50.21
2	$-NH(CH_2)_9NHCO(CH_2)_7CO-$ . . .	163	197	12.50	7.57	49.22
3	$-NH(CH_2)_5CO-$	215	250	20.00	15.00	75.00
4	$-NH(CH_2)_6NHCO(CH_2)_4CO-$ . . .	223	265	22.22	16.14	72.63
5	$-NH(CH_2)_6NHCO(CH_2)_5CO-$ . . .	202	237	18.18	13.14	72.27
6	$-NH(CH_2)_5NHCO(CH_2)_{18}CO-$ . . .	167	170	8.69	8.14	93.67
7	$-NH(CH_2)_{10}NHCO(CH_2)_{11}CO-$ . .	172	176	9.52	8.86	93.06

TABLE 6

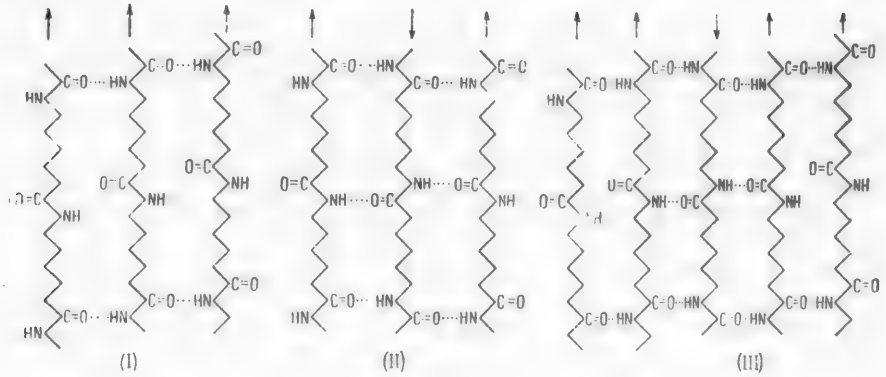
Polyamides With Heteroatoms in the Chain [15]

Acid	Diamine	Polyamide formula	Melting point
Adipic	Ethylene glycol di-(γ-aminopropyl ether	$-CO(CH_2)_4CONH(CH_2)_3O(CH_2)_2O(CH_2)_3NH-$	175°
Azeliac	The same	$-CO(CH_2)_7CONH(CH_2)_3O(CH_2)_2O(CH_2)_3(NH-$	127
Sebaic	The same	$-CO(CH_2)_8CONH(CH_2)_3O(CH_2)_2O(CH_2)_3NH-$	157
Diglycolic	Hexamethylenediamine	$-COCH_2OCH_2CONH(CH_2)_6NH-$	75
Thiodivaleric	The same	$-CO(CH_2)_4-S-(CH_2)_4CONH(CH_2)_6NH-$	180
Sulfonyldivaleric	The same	$-CO(CH_2)_4-SO_2-(CH_2)_4CONH(CH_2)_6NH-$	200
Thiodipropionic	The same	$-CO(CH_2)_2-S-(CH_2)_2-CONH(CH_2)_6NH-$	200

The stereochemical effect is even more strongly expressed in the case of polyamides of amino acids and diamines and dicarboxylic acids, containing an odd number of methylene groups. The formation of hydrogen bonds between all the amide groups becomes impossible in such "odd" polyamides due to the different steric distribution of amide groups; therefore the number of amide groups, connected by hydrogen bonds, decreases (Table 5).

From the examples given in Table 5, one can see that odd polyamides fall into three groups. The first group includes polyamides of odd diamines and odd dicarboxylic acids, which have the greatest discrepancy between the melting points found and those calculated as only 50% of the amide groups are bound by hydrogen bonds (Nos. 1 and 2 in Table 5). The second group includes polyamides of odd amino acids and of odd dicarboxylic acids with even diamines or of even dicarboxylic acids with odd diamines. The melting points found and those calculated differ greatly for this group of polyamides, though less than for the first group. This may be explained by the fact that here about 75% of the amide groups are bound by hydrogen bonds (Nos. 3, 4, 5 in Table 5). The relative amount of hydrogen bonds increases in each of these groups with an elongation of the monomer molecule and this may be most clearly seen using the third group of polyamides as an example (Nos. 6 and 7, Table 5), as, despite the presence of odd components in the chain, the melting points bound and those calculated are quite close, as the number of hydrogen bonds exceeds 90%.

In the case of ϵ-caprolactams, the actual distribution of polymer chains corresponds to the case when 75% of the amide groups form hydrogen bonds [13]. As a poly-ϵ-caprolactam molecule has a vector structure, there are three possible relative positions of the macromolecules in which different numbers of hydrogen bonds are formed. In the first case, 50% of the hydrogen bonds are formed and the melting point should be 180°; in the second case, 100% of the hydrogen bonds are formed, and the melting point should be 250°. Actually, a distribution of macromolecules probably occurs (III) which corresponds to 75% of the hydrogen bonds and m.p. 215°.



(I) (II) (III)

The introduction of an ether or sulfide link into a polyamide chain results in a fall in melting point, as can be seen from the data in Table 6.

Thus, the polyamide from decamethylenediamine and adipic acid (m.p. 230°) melts 55° higher than the polyamide from the di-γ-aminopropyl ether of ethylene glycol. The polyamide of glutaric acid and hexamethylenediamine (m.p. 240°) melts 165° higher than the corresponding polyamide of diglycolic acid. It should be noted that the introduction of two ether links does not eliminate the effect of the evenness factor as can be seen by comparing the melting points of the polyamides of ethylene glycol di-γ-aminopropyl ether with azelaic and sebacic acids.

TABLE 7

Repeating unit	Melting point
—CO—⟨⟩—COO(CH₂)₂O—	256°
—CO(CH₂)₇COO(CH₂)₂O—	47
—CO—⟨⟩—⟨⟩—COO(CH₂)₂O—	330
—CO(CH₂)₇COO(CH₂)₂O—	74
—CO—⟨⟩—⟨⟩—COO(CH₂)₆O—	195
—CO(CH₂)₇COO(CH₂)₆O—	65

The introduction of a sulfide link lowers the melting point by 20° in comparison with that of the corresponding polyamide without a thio link. However, a sulfonate group practically does not lower the melting point and its effect is equivalent to the methylene group effect.

TABLE 8

Repeating unit	Melting point
OC⟨⟩COO(CH₂)₂O	63°
—OC⟨⟩—COO(CH₂)₂O—	103
—OC—⟨⟩—COO(CH₂)₂O	256
—OC—⟨⟩—COOCH(CH₃)—CH₂—O—	106
—OC—⟨⟩—CO(OCH₂CH₂)₂O—	65
—OC—⟨⟩—CO(OCH₂CH₂)₂O—	60

In the case of polyphenyl, we have a compound which does not melt up to 500°, i.e., which is outstanding in having an exceptionally high thermal stability [16]. The reason for this lies, apparently, in the rigidity of

TABLE 9

Melting Points of Polyamides of Aromatic Components [18-20]

Starting materials: acid	Starting materials: diamine	Structural unit	Melting point
Terephthalic	Hexamethylene-diamine	$-COC_6H_4CONH(CH_2)_6NH-$	350° (decomp.)
Isophthalic	The same	$-COC_6H_4CONH(CH_2)_6NH-$	150
Phthalic	The same	$-COC_6H_4CONH(CH_2)_6NH-$	50
Adipic	o-Phenylene-diamine	$-CO(CH_2)_4CONHC_6H_4NH-$	105
	m- the same	$-CO(CH_2)_4CONHC_6H_4NH-$	258
	p- the same	$-CO(CH_2)_4CONHC_6H_4NH-$	260
Sebacic	m- the same	$-CO(CH_2)_8CONHC_6H_4NH-$	145
Adipic	Benzidine	$-CO(CH_2)_4CONHC_6H_4C_6H_4NH-$	400 (decomp.)
Sebacic	The same	$-CO(CH_2)_8CONHC_6H_4C_6H_4NH-$	375 (decomp.)
Adipic	p,p'-Diaminodi-phenylmethane	$-CO(CH_2)_4CONHC_6H_4CH_2C_6H_4NH-$ . . .	350 (decomp.)
	p,p'-Diaminodi-phenylethane	$-CO(CH_2)_4CONHC_6H_4CH_2CH_2C_6H_4NH-$.	400 (decomp.)
p,p'-Diphenyl-dicarboxylic	Hexamethylene-diamine	$-COC_6H_4C_6H_4CONH(CH_2)_6NH-$	360 (decomp.)
p,m'-Diphenyl-dicarboxylic	The same	$-COC_6H_4C_6H_4CONH(CH_2)_6NH-$	140
m,m'-Diphenyl-dicarboxylic	The same	$-COC_6H_4C_6H_4CONH(CH_2)_6NH-$	142
m,m'-Diphenyl-methanedicar-boxylic	The same	$COC_6H_4CH_2C_6H_4CONH(CH_2)_6NH-$	113

TABLE 10

Polyamides of Aromatic Acids and Diamines with Substituents in the Nucleus

Acid	Diamine	Polyamide formula	Melting point
2-Methylterephthalic	Hexamethylen-diamine	$-COC_6H_3(CH_3)CONH(CH_2)_6NH-$ . .	248°
2,5-Dimethyltere-phthalic	The same	$-COC_6H_2(CH_3)_2CONH(CH_2)_6NH-$ . .	143
2,5-Dihydroxytere-phthalic	The same	$-COC_6H_2(OH)_2CONH(CH_2)_6NH-$ . .	334 (decomp.)
Adipic	2,4-Toluylene-diamine	$-CO(CH_2)_4CONHC_6H_3(CH_3)NH-$ . .	175

the macromolecule, its dense packing, due to high symmetry, and the existence of large interchain forces. For this reason the polyesters of aromatic p-dicarboxylic acids have higher melting points than the corresponding polyesters of aliphatic dicarboxylic acids [17].

Table 7 gives the melting points of polyesters of aliphatic and aromatic acids and various glycols. The melting points of aliphatic polyesters, containing an even number of carbon atoms, are given for comparison.

From this data it can be seen that the melting point of aromatic polyesters is higher than that of aliphatic ones with the same number of carbon atoms in the chain. The highest melting points are those of polyesters in which the carboxyl is directly bonded to the aromatic nucleus. On increasing the length of the aliphatic chain of the glycol or the acid, the polyester melting point decreases, as can be seen from the data in Table 9, which gives the melting points of polyesters of terephthalic, isophthalic and phthalic acids and aliphatic glycols.

The introduction of an ether link into the glycol, as in aliphatic polyesters, results in a decrease in melting point. The side methyl group acts the same in an acid or in a glycol. The relative position of the carboxyl groups is as important, as can be seen from the data in Table 8.

The introduction of an aromatic nucleus into a polyamide molecule also results in an increase in melting point, as can be seen from the data in Table 9, which gives the melting points of polyamides with aromatic nuclei in the chain.

As can be seen from these data, a particularly high increase in melting point is observed in the case of aromatic para-dicarboxylic acids of the terephthalic types of aromatic para-diamines. If the carboxyl groups or amino groups are in the meta or ortho positions, this results in a large decrease in melting point.

The presence of substituents in the aromatic nuclei of dicarboxylic acids and diamines results in a decrease in melting point, as can be seen from the data in Table 10.

The hydroaromatic diamines are also very effective. The pertinent data are given in Table 11.

TABLE 11

Polyamides With Hydroaromatic Units

Acid	Diamine	Polyamide formula	Melting point
Hexahydroterephthalic	Hexamethylenediamine	$-COC_6H_{10}CONH(CH_2)_6NH-$	360° (decomp.)
Adipic	1,4-Diaminocyclohexane	$-CO(CH_2)_4CONHC_6H_{10}NH-$	400 (decomp.)
m,m-Diphenyldicarboxylic	The same	$-COC_6H_4C_6H_4CONHC_6H_{10}NH-$ . . .	390
m,m-Diphenylmethanedicarboxylic	The same	$-COC_6H_4CH_2C_6H_4CONHC_6H_{10}NH-$.	174

SUMMARY

By changing separate characteristics of the macromolecular structures of polyamides and polyesters it is possible to change greatly their properties in various directions. The properties of the polymers obtained, in particular their melting points, depend on the capacity of the units of the macromolecules for dense packing into a crystalline modification, which is primarily determined by the structural symmetry of the unit and, consequently, by the structure of the starting materials. A capacity for crystallization leads to high melting points and high stability of the fibers formed. The presence of hydrogen bonds and polar groups, which increases the forces of macromolecular reactions, has a certain effect in the same direction.

Due to a high degree of symmetry, paraphenylene units in a macromolecule are readily packed into a crystal and facilitate the formation of stable, high melting polymers. Hydrogenated paraphenylene units (trans-isomers) are only slightly inferior to them in their capacity for crystallization and form almost as high melting polymers.

The presence of such factors as ether links, sulfide links, side alkyl and aryl groups, as well as meta- and ortho-placing of the functional groups in aromatic derivatives makes crystallization more difficult and the polymers more prone to transition into the amorphous state.

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A NEW METHOD FOR SYNTHESIZING THE ESTERS OF PHOSPHINIC AND THIOPHOSPHINIC ACIDS

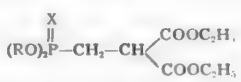
XXVII. ADDITION OF DIALKYLPHOSPHOROUS AND DIALKYLTHIOPHOSPHOROUS ACIDS TO IDENE DERIVATIVES OF MALONIC ESTER AND ACETYLACETONE. PHOSPHONBARBITURIC ACIDS.

A. N. Pudovik and T. M. Moshkina

As we showed previously, phosphonalkylmalonic esters may be readily synthesized by adding malonic ester and its homologs to vinylphosphinic ester [1] or by adding dialkylphosphorous acids to idene derivatives of malonic ester [2]. Both of these methods were also used successfully for synthesizing phosphonalkylacetoacetic esters. In developing andextending this work, we investigated the addition of dimethyl-, diethyl- and di-n-butylphosphorous and diethylthiophosphorous acids to methylene-malonic ester and to some acetylacetone diene derivatives. The additions to methylenemalonic ester were carried out in the presence of alkali metal alcoholates by the method described previously [3]; they proceeded very readily, with a considerable heat effect, and gave dialkylphosphonmethyl- and dialkylthiophosphonmethylmalonic esters in satisfactory yields (Table 1).

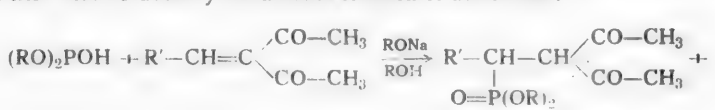
TABLE 1

Diethyl Esters of Dialkylphosphonmethyl and Dialkylthiophosphonmethyl-malonic Acids



R	X	Yield (in %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Phosphorous content (in %) found	Phosphorous content (in %) calc.
CH_3	O	88	172—173° (11)	1.4424	1.2034	62.03	62.54	11.64	10.99
C_2H_5	O	71	179—180 (10)	1.4355	1.1278	71.76	71.78	10.02	10.00
n-C_4H_9	O	46	204—205 (14)	1.4410	1.0750	89.93	90.25	8.59	8.47
C_2H_5	S	51	180—182 (11)	1.4570	1.1123	79.86	79.21	9.33	9.50

As a result of the addition of dialkylphosphorous acids to ethylidene and benzilideneacetylacetone, in the presence of an alcohol solution of alkali metal alcoholates, we obtained ketophosphinic esters, rather than phosphonethyl and phosphonbenzyl derivatives of acetylacetone. Apparently, the normal addition products that were formed at first were cleaved by the alcohol solution of alcoholate:



$$+ ROH \xrightarrow{RONa} (RO)_2\overset{O}{\overset{\|}{P}}-CH(R')-CH_2-CO-CH_3 + CH_3COOR$$

where $R = CH_3, C_2H_5, n\text{-}C_4H_9$ & $R' = CH_3$ & C_6H_5.

The ketophosphinic esters obtained by this method, were found to be identical with those synthesized previously by the addition of dialkylphosphorous acids to α,β-unsaturated ketones [4]. Phosphonethyl and phosphonbenzyl derivatives of acetylacetone were prepared in good yields by the addition of dialkylphosphorous acid to ethylidene- and benzylidene-acetylacetone in the presence of dry alcoholates. In this case the addition products were not cleaved. The constants of the α-(dialkylphosphon)-ethyl- and dialkylphosphonbenzylacetylacetones are given in Table 2. We illustrated the capacity of dialkylphosphonbenzylacetylacetones for cleaving

TABLE 2

α-(Dialkylphosphon)-ethyl- and Dialkylphosphonbenzylacetylacetones

$$(RO)_2\overset{O}{\overset{\|}{P}}-\overset{R'}{\overset{|}{CH}}-CH\begin{matrix}CO-CH_3\\CO-CH_3\end{matrix}$$

R	R'	Yield (in %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Phosphorous content (in %) found	Phosphorous content (in %) calc.
CH_3	C_6H_5	40	198—200° (5)	1.5388	—	—	—	10.06	10.40
C_2H_5	C_6H_5	35	200—202 (5)	1.5178	1.1790	83.62	83.18	9.59	9.50
$n\text{-}C_4H_9$	C_6H_5	42	206—207 (4)	1.4970	1.1060	101.0	101.6	8.54	8.11
C_2H_5	CH_3	50	170—172 (13)	1.4750	1.1690	63.60	63.89	12.18	11.74

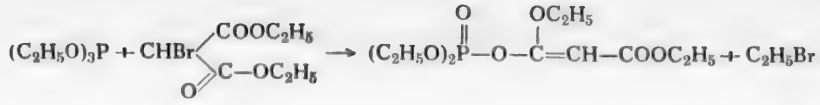
readily when treated with alcoholate in alcohol solution by a special experiment using diethylphosphonbenzylacetylacetone as the example. We obtained 1-phenyl-1-diethylphosphonbutanone-3.

The dialkylphosphonmethylmalonic esters synthesized in this work and the α-(dialkylphosphon)-ethyl- and dialkylphosphonbenzylmalonic esters we prepared previously, were used for the synthesis of phosphonbarbituric acid derivatives. This type of compound may be valuable from the point of view of physiological activity. The phosphonbarbituric and phosphonthiobarbituric acids were synthesized by the usual method used for the synthesis of barbituric acids, namely by heating phosphonalkyl- or phosphonbenzylmalonic esters in an alcohol solution with urea or thiourea in the presence of sodium alcoholate.

$$(RO)_2\overset{O}{\overset{\|}{P}}-CH(R')-CH\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix} + \begin{matrix}H_2N\\H_2N\end{matrix}>CO \xrightarrow{C_2H_5ONa} (RO)_2\overset{O}{\overset{\|}{P}}-\overset{R'}{\overset{|}{CH}}-CH\begin{matrix}CO-NH\\CO-NH\end{matrix}>CO$$

where $R = CH_3, C_2H_5, n\text{-}C_4H_9$ & $R' = H, CH_3, C_6H_5$

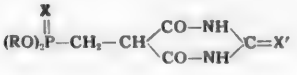
The reaction with thiourea proceeded in an analogous direction. The yield of phosphonbarbituric and phosphonthiobarbituric acids was 60-70%. The characteristics of the products obtained are given in Tables 3 and 4. We then decided to synthesize phosphonbarbituric acids, in which phosphorous of the phosphinic groups is directly bonded to the carbon of the pyrimidine ring. It seemed that the simplest way to prepare the phosphonmalonic ester required for the synthesis was by obtaining it from bromo- or chloro-malonic esters by treating them with triethylphosphite by an Arbuzov reaction. A. E. Arbuzov, G. Kh. Kamai [5] and Kosolapoff [6] had carried out such a synthesis of phosphonmalonic ester. However, Allen and Johnson [7] considered that the triethylphosphite reaction with bromo- and dibromomalonic esters proceeded, not by the Arbuzov rearrangement scheme, but anomalously, by the equation:



To elucidate this problem, we synthesized phosphonmalonic ester by various methods: by treating bromo- and chloromalonic esters with triethylphosphite and by treating sodiomalonic ester with the acid chloride of diethylphosphoric acid. The products obtained in all cases had identical constants. Phosphonmalonic esters,

TABLE 3

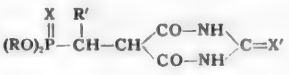
Dialkylphosphonmethyl- and Dialkylthiophosphonmethylbarituric and -Thiobarbituric Acids



R	X	X'	Melting point	Phosphorous content (in %)	
				found	calculated
CH_3	O	O	97°	12.31	12.40
C_2H_5	O	O	100	10.74	11.15
n-C_4H_9	O	O	109	9.31	9.28
C_2H_5	S	O	98-100	9.99	10.50
CH_3	O	S	161	11.40	11.65
C_2H_5	O	S	162-163	9.95	10.54
n-C_4H_9	O	S	168	8.84	8.85
C_2H_5	S	S	163-164	10.79	10.99

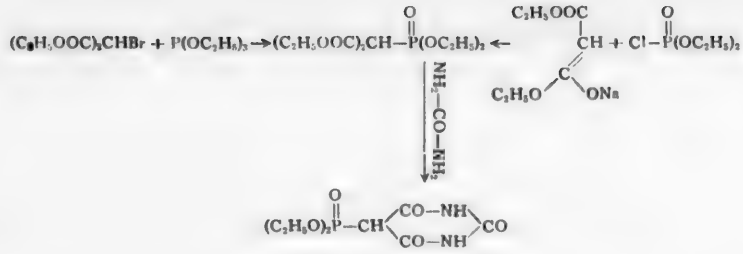
TABLE 4

Dialkylphosphon- and Dialkylthiophosphonethyl-, Dialkylphosphon- and Dialkylthiophosphonbenzylbarbituric and -Thiobarbituric Acids



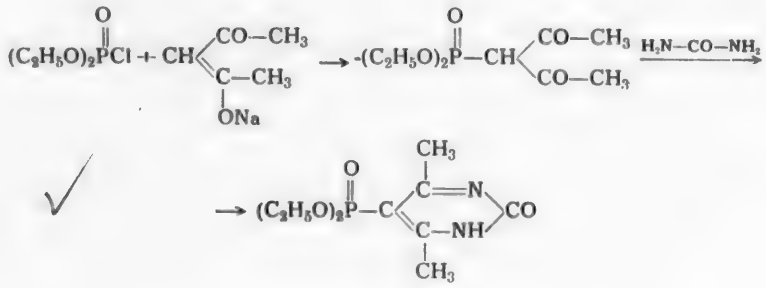
R	R'	X	X'	Melting point	Phosphorous content (in %)	
					found	calculated
CH_3	CH_3	O	O	105°	11.52	11.75
C_2H_5	CH_3	O	O	107	10.06	10.61
n-C_4H_9	CH_3	O	O	110	8.65	8.90
C_2H_5	CH_3	S	O	144	9.63	10.06
CH_3	CH_3	O	S	177	11.03	11.07
C_2H_5	C_6H_5	O	O	109	8.60	8.75
C_2H_5	C_6H_5	S	O	110	7.99	8.38
C_2H_5	C_6H_5	O	S	178	8.82	8.38
C_2H_5	C_6H_5	S	S	179	7.69	8.03

obtained by both methods, reacted with urea to give the same phosphonbarbituric acid with m.p. 97-98°. A mixed melting point of the two samples was not depressed. The results obtained did not confirm Allen and Johnson's conclusion on the anomalous course of the reaction of bromomalonic ester with triethylphosphite. The reaction proceeded by the usual scheme of Arbuzov rearrangement.



We decided to synthesize phosphonacetylacetone, as well, similarly to phosphonmalonic ester.

As we showed previously, diethylphosphonacetylacetone cannot be prepared by treating halogen-substituted derivatives of acetylacetone with triethylphosphite, as in this case the reaction proceeds by an anomalous mechanism with the formation of an unsaturated ester [8]. Therefore, we used another method for synthesizing phosphonacetylacetone – treating the acetylacetone sodio derivative with the acid chloride of diethylphosphoric acid. The diethylphosphonacetylacetone thus obtained was then condensed with urea. The reaction proceeded by the equation



While carrying out these investigations we became acquainted with the work of Goldhahn and Fiebig [9]. They have synthesized a series of β-(dialkylphosphon)-ethyl derivatives of barbituric and thiobarbituric acids, starting from esters of vinylphosphinic acid. Using the method we developed previously, they prepared the addition products of malonic ester and its homologs and vinylphosphinic ester and condensed them with urea and thiourea.

EXPERIMENTAL

Addition of dialkylphosphorous and dialkylthiophosphorous acids to methylenemalonic ester. Methylenemalonic ester was prepared by the method of R. Ya. Levina and N. N. Godovikov [10]. A saturated solution of sodium alcoholate was gradually added to 10-12 g of methylenemalonic ester and the dialkylphosphorous or dialkylthiophosphorous acid, in an equimolecular amount. The alcoholate was prepared from the alcohol with the same radical as that contained in the ester groups of the dialkylphosphorous or dialkylthiophosphorous acids. The addition of the alcoholate produced strong heating up of the reaction mixtures (to 70-90°). After a short heating on a water bath (15-20 minutes) the reaction mixtures were distilled in vacuum. The constants and analyses of the products synthesized are given in Table 1. The esters of dialkylphosphonmethylmalonic acid were colorless liquids without smell. Diethylthiophosphonmethylmalonic ester was a pale yellow liquid with an unpleasant smell.

Addition of diethylphosphorous acid to benzylideneacetylacetone. Experiment 1. A solution of sodium ethylate in ethyl alcohol was added dropwise to a mixture of 10 g of benzylideneacetylacetone and 11 g of diethylphosphorous acid. A considerable induction period was observed. Then the temperature of the reaction mixture quickly rose to 70°. As a result of two distillations, we isolated 4.2 g of 1-phenyl-1-diethylphosphonbutanone-3 with b.p. 190-191° at 8 mm, n_D^{20} 1.5005, d_4^{20} 1.1264.

Experiment II. A small amount of dry sodium ethylate was added to a mixture of 10 g of benzylideneacetylacetone and 11 g of diethylphosphorous acid. The reaction mixture heated up strongly. After heating for 30 minutes on a water bath, the reaction mixture was distilled in vacuum. As a result of two distillations, we obtained 6.9 g of diethylphosphonbenzylacetylacetone with b.p. 200-202° at 5 mm, n_D^{20} 1.5178, d_4^{20} 1.1790.

Addition of dimethylphosphorous acid to benzylideneacetylacetone. The reaction was carried out with 13 g of benzylideneacetylacetone and 13 g of dimethylphosphorous acid with dry sodium methylate. We obtained 8.5 g of dimethylphosphonbenzylacetylacetone as a very viscous liquid with b.p. 198-200° at 5 mm, n_D^{20} 1.5388.

Cleavage of diethylphosphonbenzylacetylacetone. A solution of 4 g of diethylphosphonbenzylacetylacetone in ethyl alcohol, containing a small amount of sodium ethylate, was heated on a water bath for 2 hours. On distilling, we obtained 2.3 g of 1-phenyl-1-diethylphosphonbutanone-3 with b.p. 190-192° at 8 mm, n_D^{20} 1.5030, d_4^{20} 1.1294.

General method of synthesizing phosphonbarbituric acids. To a solution of 0.03-0.04 mole of sodium ethylate in 20-30 ml of dry ethyl alcohol was added 0.07 mole of urea or thiourea and 0.01 mole of the appropriate dialkylphosphonmethyl-, dialkylphosphonethyl- or dialkylphosphonbenzylmalonic ester or their thioanalogs. The reaction mixture was heated under reflux on an oil bath for 6-7 hours. The sodium salt of the barbituric acid, which precipitated, was dissolved in water; the solution was acidified with dilute hydrochloric acid. After filtration, the solution was concentrated in vacuum. The crystals of the phosphonbarbituric acids deposited were recrystallized from alcohol.

Synthesis of diethylphosphonmalonic ester. Experiment I. A mixture of 16.6 g of triethyl phosphite and 23.9 g of bromomalonic ester was heated on a water bath for 3 hours. As a result of distilling the reaction mixture, we obtained 17 g of phosphonmalonic ester with b.p. 160-161° at 10 mm, n_D^{20} 1.4420, d_4^{20} 1.1660. According to the data in [5] it has b.p. 154-156° at 3-4 mm, n_D^{20} 1.4450, d_0^0 1.1790.

Experiment II. A mixture of 13.5 g of triethyl phosphite and 16 g of chloromalonic ester obtained had b.p. 160-161° at 10 mm, n_D^{20} 1.4410, d_4^{20} 1.1644.

Experiment III. Sodiomalonic ester was prepared in ether solution from 1.3 g of sodium and 9.2 g of malonic ester. After adding 10 g of the acid chloride of diethylphosphoric acid, the reaction mixture was heated on a water bath for 10 hours. The precipitate of sodium chloride was filtered off and on distilling the residue, we obtained 5 g of phosphonmalonic ester with b.p. 159-160° at 10 mm, n_D^{20} 1.4458.

Found %: P 10.59. $C_{11}H_{21}O_7P$. Calculated %: P 10.50.

Synthesis of diethylphosphonbarbituric acid. Experiment I. The reaction was carried out with 1.4 g of diethylphosphonmalonic ester, prepared from bromomalonic ester, and 2 g of urea. We obtained 0.46 g of diethylphosphonbarbituric acid. The m.p. was 97°.

Found %: P 12.04. $C_8H_{13}O_6PN_2$. Calculated %: P 11.74.

Experiment II. Similarly, from a reaction with diethylphosphonmalonic ester, prepared from the acid chloride of diethylphosphoric acid and sodiomalonic ester, we obtained 0.5 g of diethylphosphonbarbituric acid with m.p. 98°.

Found %: P 12.74. $C_8H_{13}O_6PN_2$. Calculated %: P 11.74.

A mixed sample of the diethylphosphonbarbituric acids from both experiments had m.p. 97-98°.

Synthesis of diethylphosphonacetylacetone. 15 g of the acid chloride of diethylphosphoric acid was added to the sodio derivative of acetylacetone, prepared in ether solution from 2 g of sodium and 10 g of acetylacetone. The reaction mixture was heated on a water bath for 12 hours. The precipitate of sodium chloride was filtered off, the ether distilled off and the residue distilled in vacuum. We obtained 5.3 g of diethylphosphonacetylacetone with b.p. 161-162° at 10 mm, n_D^{20} 1.4328.

Found %: P 12.82, 12.93. $C_9H_{17}O_5P$. Calculated P 13.13.

Reaction of diethylphosphonacetylacetone with urea. The reaction was carried out in dioxane solution with 3 g of urea, 2 g of diethylphosphonacetylacetone in the presence of dry sodium ethylate. The mixture was heated under reflux on an oil bath for 10 hours. The precipitate formed was dissolved in water, the solution

treated with dilute hydrochloric acid and the product deposited on evaporating off the water, recrystallized from alcohol. We obtained 0.4 g of a crystalline product with m.p. 115-117°.

Found %: P 11.75, 11.90. $C_{10}H_{17}O_4N_2P$. Calculated %: P 11.92.

SUMMARY

1. Dialkylphosphorous and dialkylthiophosphorous acids readily added to methylenemalonic ester and ethylidene- and benzylideneacetylacetone in the presence of alkali metal alcoholates. It was established that the addition reaction to idene derivatives of acetylacetone must be carried out in the presence of dry alcoholates to avoid cleavage of the addition products.

2. A series of phosphonalkyl derivatives of barbituric and thiobarbituric acids were synthesized by reacting phosphon-, phosphonmethyl-, phosphonethyl- and phosphonbenzylmalonic esters with urea and thiourea.

3. It was shown that the reaction between triethylphosphite and bromomalonic ester proceeds by an Arbuzov rearrangement scheme, and not by an anomalous mechanism, as considered by Johnson and Allen.

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A NEW METHOD FOR SYNTHESIZING THE ESTERS OF PHOSPHINIC AND THIOPHOSPHINIC ACIDS

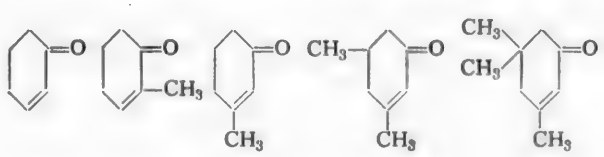
XXVIII. THE REACTIONS OF PARTIAL ESTERS OF PHOSPHORUS ACIDS WITH α,β-UNSATURATED CYCLIC KETONES AND CYCLOHEXENYL ACETATE

A. N. Pudovik and I. V. Konovalova

Cyclic ketophosphinic and ketothiophosphinic esters with the ketone group in the ring have up to now been a difficultly accessible group of organophosphorus compounds. The most general method of Arbuzov rearrangement does not give positive results when applied to cyclic α-haloketones: as one of us showed, the reactions in this case proceed by an anomalous mechanism and lead to unsaturated phosphonic esters [1]. The reactions of β- and γ-haloketones of the alicyclic series with phosphorous esters have not been investigated, but by analogy with the reactions of secondary alkyl halides [2] and aliphatic γ-haloketones [3], it may be assumed that either they cannot be accomplished or proceed with the elimination of hydrogen halide. The Michaelis-Baker method as applied to α-haloketones of the aliphatic and cyclic series has hardly been investigated as yet, the reactions in most cases are complicated, forming mixtures of various products; the mechanism of these reactions requires further study.

In a series of works we showed that ketophosphinic esters of the aliphatic series may be readily obtained by the addition of partial esters of phosphorus acids to α,β-unsaturated ketones of various structures [4]. This method may also be used when the double bond is in a ring, as we found in the case of acetylcyclohexene.

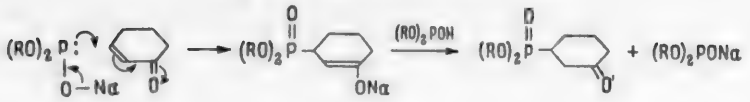
In the present work we investigated the addition of dialkylphosphorous and dialkylthiophosphorous acids to a series of cyclic α,β-unsaturated ketones, containing a ketone group and a double bond in a ring.



The reactions were carried out by the usual method, in the presence of alkali metal alcoholates. Dimethylphosphorous, diethylphosphorous and diethylthiophosphorous acids were added. Of all the ketones used, cyclohexenone was found to be the most reactive; the reaction with it proceeded in the presence of a very small amount of sodium alcoholate, the induction period was very short and the reaction mixture temperature rose during the reaction to 110-130°. As the number of substituents increased in the ring, the reactivity of the unsaturated ketones decreased; to achieve the reaction with isophorone, the reaction mixture had to be heated on an oil bath for several hours in the presence of a large quantity of alcoholate; the reaction did not proceed without heating.

The ketophosphinic esters obtained were not oxidized by potassium permanganate in the cold and did not add bromine. This showed that they did not contain double bonds; the addition occurred at the carbon-carbon double bond, and not at the carbonyl group.

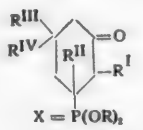
$$(RO)_2POH + RONa \rightleftharpoons (RO)_2PONa + ROH$$



The characteristics of the products obtained are given in the table.

From the hydrolysis of the series of esters synthesized, we could not obtain the corresponding ketophosphinic acids in a crystalline state. All of them were straw colored, viscous liquids.

Esters of Cyclohexanonephospninic and Cyclohexanonethiophosphinic Acids



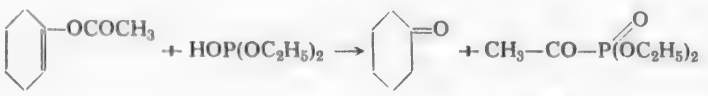
Substituents						Yield (in %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Phosphorous content (in %)	
R	R^I	R^{II}	R^{III}	R^{IV}	X					found	calc.	found	calc.
C_2H_5	H	H	H	H	O	54	170° (15)	1.4620	1.1210	57.40	57.05	12.95	13.24
CH_3	H	H	H	H	O	46	160 (10)	1.4723	1.2131	47.56	47.81	14.89	15.04
C_2H_5	H	H	H	H	S	57	182 (15)	1.4998	1.1307	64.95	64.54	12.18	12.40
CH_3	CH_3	H	H	H	O	66	162 (8)	Crystals, m.p.			96°	14.31	14.09
C_2H_5	CH_3	H	H	H	O	50	166 (8)	1.4612	1.1007	61.89	61.66	12.77	12.50
C_2H_5	CH_3	H	H	H	S	60	165 (8)	1.4936	1.1099	69.13	69.16	11.77	11.74
CH_3	H	CH_3	H	H	O	47	162 (11)	1.4721	1.1801	52.22	52.44	14.03	14.09
C_2H_5	H	CH_3	H	H	O	54	167 (11)	1.4653	1.1130	61.73	61.67	12.51	12.50
C_2H_5	H	CH_3	H	H	S	53	172 (9)	1.4950	1.1182	68.89	69.16	12.10	11.74
C_2H_5	CH_3	H	CH_3	H	O	59	162 (8)	1.4610	1.0810	66.52	66.29	12.23	11.87
CH_3	CH_3	H	CH_3	H	O	60	165 (8)	1.4780	1.1499	57.61	57.05	13.33	13.24
C_2H_5	CH_3	H	CH_3	H	S	66	173 (9)	1.4921	1.0940	73.72	73.77	11.50	11.15
$n\text{-}C_4H_9$	CH_3	H	CH_3	H	O	59	196 (8)	1.4580	1.0189	85.17	84.76	9.83	9.74
C_2H_5	H	CH_3	CH_3	CH_3	O	60	167 (8)	1.4641	1.0710	71.20	70.90	11.36	11.23

We showed previously that the simplest ester of an unsaturated alcohol – vinyl acetate – adds very readily to dialkylphosphorous and dialkylthiophosphorous acids [5] and acid esters of alkyl- and aryl-phosphinic acids [6], to form β-phosphonethyl acetates.

$$CH_2{=}CH{-}OCOCH_3 + HOP(OR)_2 \rightarrow (RO)_2\overset{\overset{O}{\|}}{P}{-}CH_2{-}CH_2OCOCH_3$$

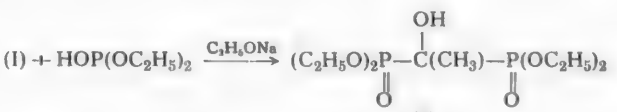
We thought it would be interesting to extend this reaction to esters of unsaturated cyclic alcohols. In this investigation we used the acetates of cyclohexenol and 2-methylcyclohexenol. The reactions of dialkylphosphorous and dialkylthiophosphorous acids in the presence of alkali metal alcoholates proceeded very vigorously. As a result of the reactions of diethylphosphorous acid with both acetates, we obtained high boiling products that had identical constants, and cyclohexanone and methylcyclohexanone, respectively. An analogous picture was observed, as well, in carrying out the reaction with diethylthiophosphorous acid.

The phosphorous content of the high boiling products was approximately 6-7% higher than that expected in normal addition products. It is known from the patent [7] that in the presence of an alkali metal or tertiary amine, vinyl acetate is capable of acetylating secondary alcohols of the type RR'CHOH, where: R—CN, CH_2CN, CH_2OH, CH_2Cl etc. and R' is an alkyl or aryl radical. Apparently, in the reactions we investigated, instead of additions, here, also, the reaction proceeded first through the acetylation of dialkylphosphorous and dialkylthiophosphorous acids by the acetate.

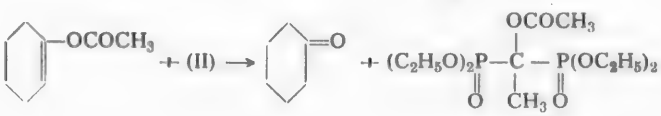


(I)

The ketophosphinic ester (I) then added dialkylphosphorous acid with the formation of methyldi-(diethylphosphon)-carbinol (II), which was again acetylated by cyclohexenyl acetate.



(II)



(III)

Thus, the final reaction product was the acetate of methyldi-(diethylphosphon)-carbinol (III). The analysis and molecular refraction data of the products obtained coincide with those calculated theoretically for (III).

The compound (III) had previously been prepared by A. E. Arbuzov and M. M. Azanovskaya [8] by treating acetyl chloride with sodium diethylphosphite. The constants of the substances obtained by them and by us were identical. To confirm the proposed reaction mechanism, we added diethylphosphorous acid to acetophosphinic ester (I). This reaction proceeded very readily, and substance (II) was obtained in 61% yield. Its composition was found to be different from that of substance (III); the hydroxyl group was quantitatively determined in substance (II), while it was absent in (III); the constants of substances (II) and (III) differed little. Results, analogous to those described above, were also obtained with diethylthiophosphorous acid. Thus, we showed that the reaction of vinyl acetate and cyclohexenyl and methylcyclohexenyl acetates with dialkylphosphorous and dialkylthiophosphorous acids in the presence of alkali metal alcoholates proceeded differently; vinyl acetate added the partial esters of phosphorus acids, while the acetates of cyclic unsaturated alcohols acetylated them.

EXPERIMENTAL

Addition of alkylphosphorous and dialkylthiophosphorous acids to cyclic, unsaturated ketones. The reactions were performed with equimolecular amounts of the unsaturated ketones and the dialkylphosphorous or dialkylthiophosphorous acids in the presence of alkali metal alcoholates. After various induction periods for the different ketones, the reactions began and proceeded with considerable evolution of heat. The more substituent groups the ketones contained, the longer the induction period and the greater the amount of catalyst required to complete the reaction. In most reactions the temperature of the reaction mixture rose to 90-100°. After neutralization of the sodium alcoholate with glacial acetic acid, the reaction mixture was distilled in vacuum.

Reaction of Δ'-cyclohexenyl acetate with diethylphosphorous acid. A saturated alcoholic solution of sodium ethylate was added dropwise to a reaction mixture consisting of 10.5 g of diethylphosphorous acid and 10.5 g of cyclohexenyl acetate, in an Arbuzov flask. The temperature of the liquid rose to 128°. On cooling,

the reaction mixture was neutralized with glacial acetic acid. As a result of two distillations, we obtained 5 g of cyclohexanone and 13 g of the acetate of methyl-di-(diethylphosphon)-carbinol (III).

Cyclohexanone. B.p. 39-40° (7.5 mm), d_4^{20} 0.9484, n_D^{20} 1.4481, MR_D 27.67; calc. 27.72. semicarbazone m.p. 164°, 2,4-dinitrophenylhydrazone m. p. 160°. Literature data: b.p. 47° (15 mm), d_4^{20} 0.9478, n_D^{20} 1.4507; semicarbazone m.p. 165°; 2,4-dinitrophenylhydrazone m.p. 160°.

Methyl-di-(diethylphosphon)-carbinol. B.p. 174-175.5° (7 mm), d_4^{20} 1.1511, n_D^{20} 1.4308, MR_D 80.80; calc 81.00.

Found %: P 17.70, 17.66. $C_{12}H_{26}O_6P_2$. Calculated %: P 17.22.

It did not contain hydroxyl groups and did not react with benzoyl chloride.

Reaction of Δ'-methylcyclohexenyl acetate with diethylphosphorous acid. The reaction was similar to that described, with 6.9 g of diethylphosphorous acid and 7.7 g of Δ'-methylcyclohexenyl acetate in the presence of sodium ethylate. As a result of distilling the reaction mixture, we isolated 4.1 g of methylcyclohexanone with b.p. 54-55° (14 mm) and 10.5 g of the acetate of methyl-di-(diethyl-phosphon)-carbinol with b.p. 174° (8 mm); d_4^{20} 1.1518, n_D^{20} 1.4310.

Found %: P 17.68. $C_{13}H_{30}O_6P_2$. Calculated %: P 17.22.

Addition of diethylphosphorous acid to the diethyl ester of acetophosphinic acid. A saturated alcohol solution of sodium ethylate was added dropwise to a reaction mixture of 19 g of acetophosphinic ester, prepared from the data in [9], and 15 g of diethylphosphorous acid. The reaction mixture heated up strongly (to 130°). We obtained 20 g of methyl-di-(diethylphosphon)-carbinol.

B.p. 180°C (9.5 mm), d_4^{20} 1.1535, n_D^{20} 1.4300, MR_D 71.45; calc. 71.61.
Found %: P 19.33; OH 5.11. $C_{10}H_{24}O_7P_2$. Calculated %: P 19.49; OH 5.34.

1.4331 g of benzoyl chloride, 1.3378 g of dimethylaniline and 1.1900 g of methyl-di-(diethylphosphon)-carbinol were heated in a thermostat at 50° for 1 hour. 5.8% benzoylation occurred.

Reaction of Δ'-cyclohexenyl acetate with diethylthiophosphorous acid. The reaction was carried out with 6.3 g of Δ'-cyclohexenyl acetate and 7 g of diethylthiophosphorous acid in the presence of sodium ethylate. As a result of distilling the reaction mixture, we obtained 3 g of cyclohexanone and 9.8 g of the acetate of methyl-di-(diethylthiophosphon)- carbinol.

B.p. 169° (8 mm), d_4^{20} 1.1421, n_D^{20} 1.4710, MR_D 96.45; calc. 95.98.
Found %: P 16.77. $C_{12}H_{26}O_6P_2S_2$. Calculated %: P 16.07.

Reaction of Δ'-methylcyclohexenyl acetate with diethylthiophosphorous acid. The reaction was carried out with 7.5 g of the acetate and 7.5 g of the acid as described in the previous experiment. We obtained 4.2 g of methylcyclohexanol and 8 g of the acetate of methyl-di-(diethylthiophosphon)-carbinol with b.p. 168-170° (8 mm), d_4^{20} 1.1410, n_D^{20} 1.4710.

Found %: P 16.15, 16.37. $C_{12}H_{26}O_6P_2S_2$. Calculated %: P 16.07.

SUMMARY

1. We added dialkylphosphorous acids and diethylthiophosphorous acid to α,β-unsaturated cyclic ketones – cyclohexenone and methyl-, dimethyl- and trimethylcyclohexenone. The addition products – cyclic ketophosphinic esters – were obtained in 50-60% yields.

2. It was shown that in the presence of alkali metal alcoholates Δ'-cyclohexenyl acetate and Δ'-methylcyclohexenyl acetate did not add dialkylphosphorous and dialkylthiophosphorous acids, but acetylated them. As a result of further reactions the acetates of methyl-di-(dialkylphosphon)- and methyl-di-(dialkylthiophosphon)-carbinols were formed.

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REACTIONS OF KETONES WITH AMMONIA SOLUTIONS OF SILVER OXIDE. II

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As we established previously [1], aliphatic-aromatic ketones of the type $ArCH_2COR$ react with unexpected facility with ammonia solutions of silver oxide, forming metallic silver and products of an unknown nature. This shows that, contrary to the opinion quite widely expressed in the literature, an ammonia solution of silver oxide is not a specific reagent for the differentiation of aldehydes and ketones. Data on further investigations of this unusual reaction are given in this report.

First of all, we considered it advantageous to supplement the earlier detailed investigation [1] of methyl benzyl ketone (MBK) by an investigation of dibenzyl ketone (DBK), which can be obtained in a crystalline state and reliably purified. We found that DBK reacted with an ammonia solution of silver oxide (designated Ag_2O further on) similarly to MBK, but the reaction proceeded for a longer time and the consumption of oxidant under identical conditions was much greater in the reaction with DBK than with MBK. It can be seen from the data given in the table and in Fig. 1, that at room temperature the reaction with DBK was still not

Consumption of Ag_2O in Reactions with Dibenzyl Ketone, Methyl Benzyl Ketone and Phenylacetylcarbinol

Concentration of oxidizing solution (in g equiv/ml · 10^{-4})			Initial molar ratio Ag_2O : ketone (or ketoalcohol)	Temperature	Time (in hrs.)	Consumption of Ag_2O in moles/mole of ketone or ketoalcohol)
Ag	NH_4OH	NaOH				
		Dibenzyl ketone				
1.02	5.4	1.18	3.2 *	~18°	94	1.0
1.02	5.4	1.18	3.2 *	~18	227	1.7
0.84	4.4	0.84	2.5 *	40	3.5	1.9
1.08	5.3	1.25	2.9 *	40	4.5	2.4
1.16	4.3	1.48	3.9 *	40	3.75 **	3.0
		Methyl benzyl ketone				
0.42	2.7	0.55	3.14	38—39	2 ***	0.71
0.42	2.7	—	3.03	38—39	2 ***	0.65
0.60	4.0	0.67	5.1 *	~18	70 ***	0.70
0.60	4.0	0.67	5.15 *	~18	70 ***	0.70
0.60	4.0	0.67	4.9 *	40	2 ***	0.67
0.60	4.0	0.67	4.85 *	40	2 ***	0.70
0.62	4.2	0.62	3.50 *	52	2.5	0.72
0.62	4.2	—	3.56 *	52	2.5	0.72
		Phenylacetylcarbinol				
1.02	5.4	1.18	3.0	~18	94	2.0
1.02	5.4	1.18	3.0	~18	227	2.5
1.18	5.1	1.17	3.1	~18	66	2.2
				40	10	

* The reaction was carried out with a sample of ketone, dissolved in alcohol.

** After heating, the solution was kept in the thermostat until cool and then kept 3 more days at room temperature.

*** On keeping the reaction mixture at room temperature for a further 3-5 days, there was no Ag_2O consumption.

complete after 227 hours, while at the same time, 47-72 hours were sufficient for MBK [1]; at 40° the corresponding periods of time were about 4.5 and 1.5 hours. A small amount of benzoic acid was formed in the reaction of DBK with Ag_2O, i.e., to a certain degree, destructive processes occur; this apparently, would explain why the completion of DBK reaction with Ag_2O was not expressed clearly, when the mixture was kept for a long time Ag_2O continued to be consumed slowly, which was not observed in the case of MBK. Special experiments showed that in using freshly prepared MBK there was no benzoic acid in the reaction products with Ag_2O. About twice as much Ag_2O was consumed in a reaction with DBK as in a reaction with MBK, i.e., the amount is approximately proportional to the number of CH_2 groups between the carbonyl group and the benzene nuclei; this agrees with the results of the preceding investigation [1], which showed that only ketones containing such groups reacted readily with Ag_2O. Hence, in the reactions investigated the ketones did not react in an enol form, as in this case the Ag_2O consumption for DBK and MBK would have been the same, as in both ketones only one enol grouping can be formed.

$$C_6H_5-CH=\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}-CH_2-C_6H_5 \qquad C_6H_5-CH=\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}-CH_3.$$

The second problem in this work was to derive experiments for elucidating the mechanism of the reaction investigated. First of all, it was interesting to check whether it was possible to establish constant ratios between the reacting ketones and Ag_2O. It was shown previously that on increasing the amount of Ag_2O in the reaction mixture from 0.23 to 3.42 mole per mole of MBK, the consumption of Ag_2O increased from 0.22 to 0.64 mole per mole of the ketone [1]. We have now established that the last consumption value of 0.64 mole of Ag_2O per mole of MBK remains practically unchanged during all the variations of reaction conditions investigated: further increase of the amount of Ag_2O per mole of ketone, change in temperature from room to 40 and 52° and change in Ag concentration in the solution. The Ag_2O consumption, also, is practically unaffected by the addition of alkali to the oxidizing solution; in spite of the fact that the reaction rate noticeably increased in the presence of alkali, this did not affect the final value of Ag_2O consumption. The pertinent experimental data are given in the table and in Fig. 2. Thus, one can take it that ~0.7 mole of Ag_2O reacts with 1 mole of MBK. We would not establish such constant relations in the case of DBK, apparently, due to the secondary processes mentioned above.

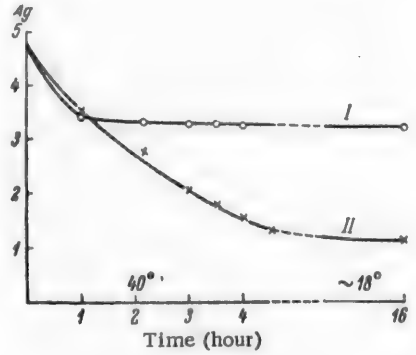

Fig. 1. The decrease of Ag in solution during the reaction of an ammonia solution of silver oxide with equimolecular amounts of methyl benzyl ketone (I) and dibenzyl ketone (II) (in milliliters of NH_4SCN solution).

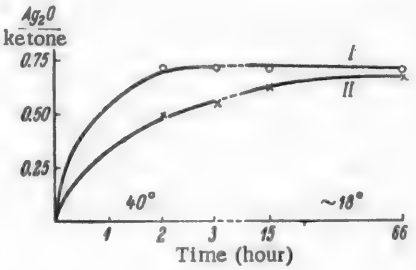

Fig. 2. Consumption of silver oxide in a reaction with methyl benzyl ketone in the presence of alkali (I) and without it (II) (in moles per mole of ketone).

We then checked experimentally the ideas put forward previously [1] on the possible directions of the reaction. Two schemes were proposed for the process: 1) first the CH_2 group, located between the benzene nucleus and carbonyl group, was oxidized and the oxidation product formed then condensed; 2) first the condensation processes occurred and then the condensation products were oxidized with Ag_2O. To check

the first hypothesis we investigated the reaction of Ag_2O with a possible first product of MBK oxidation – the keto alcohol phenylacetylcarbinol $C_6H_5-CHOH-CO-CH_3$. It is known from literature data that this keto alcohol reacts with Ag_2O to form metallic silver [2]. We established that about 2 moles of Ag_2O are consumed per mole of the keto alcohol, i.e., much more than in the reaction with MBK. Benzoic and acetic acids were the main reaction products in the oxidation of the keto alcohol, i.e., the reaction proceeded as a destructive oxidation process by the scheme

$$C_6H_5-CHOH-CO-CH_3 + 2(O) \rightarrow C_6H_5COOH + CH_3COOH$$

This may be considered as proof that the reaction of the ketone with Ag_2O does not proceed through the stage of keto alcohol formation, i.e., at first there was no oxidation of the ketone at the CH_2 group, otherwise one would expect the formation of phenylacetic acid from the ketones investigated. However, this acid was not detected in the reaction products and as far as our experiments showed, phenylacetic acid did not change at all under the conditions investigated and, presumably, there is no reason to consider it an intermediate product in the reaction of the ketones with Ag_2O. The second hypothesis that, at the beginning, condensation of the ketone occurred, was based on data from the literature: in an alkaline medium ketones are capable of condensation to form very different substances, which can be oxidized [3]. However, in our experiments the reaction proceeded in a very weakly alkaline medium. We showed previously [1] that the reaction of ketones with Ag_2O may in general proceed without the addition of alkali; however, we presumed that the alkali adsorbed on the surface of the silver oxide when it was formed, did have an effect. In the present work, we used silver oxide, known to be free from alkali (see Experimental), and were convinced that the oxidation of ketones with such a reagent occurred to the full extent, as stated above. It is very improbable that the ketone condensation occurred solely due to the effect of NH_4OH and $Ag(NH_3)_2OH$ in the dilute solutions, which we used ($\sim 10^{-1}$m). Therefore on the basis of the data obtained, one cannot consider that the reaction of ketones with Ag_2O included successive processes of oxidation and condensation or vice versa. One should consider, rather, that only one oxidative-condensation process occurred.

EXPERIMENTAL

Investigation of dibenzyl ketone. The ketone was purified through the semicarbazone and crystallized from petroleum ether, m.p. 33.5-34.5° (according to literature data, m.p. 35° [4]). To a sample of the ketone of the order of 0.2 g, dissolved in several milliliters of ethyl alcohol, was added the oxidizing solution prepared by dissolving freshly precipitated silver oxide in the minimal amount of NH_4OH and adding an amount of alkali approximately equivalent to the silver; the concentration of the components in the oxidizing solution are given in the table. Immediately, the solution blackened and metallic silver was deposited, partly in the form of a silver mirror. In the absence of alcohol the reaction proceeded more slowly. The course of the reaction was followed by determining the silver content of the solution relative to the time the reaction mixture stood. Similar experiments were also performed at 40° (± 1°).

After carrying out the reaction at 40°, the products formed were investigated. The neutral substances were extracted with ether; after evaporating off the ether a yellowish white solid (0.28 g from 0.4 g of ketone) remained; the substance was readily soluble in acetone, chloroform, dichloroethane and benzene, with difficulty in methyl alcohol, benzine and acetic acid and insoluble in water. From acetone and other solvents it was left as films on evaporation. After extracting the neutral products, the solution was evaporated, acidified with sulfuric acid and the acidic products extracted with ether; in the experiment described, we obtained 0.07 g of a solid acid, which, after crystallization from water, melted at 119-120° and did not depress the melting point of benzoic acid.

Experiments with methyl benzyl ketone. In addition to those described previously [1], here we present experiments with methyl benzyl ketone, performed in the absence of alkali and also at a raised temperature. For the experiments in the absence of alkali, the silver oxide precipitate was prepared by treating $AgNO_3$ with an insufficient amount of KOH and washing very carefully, first on a filter and then by decantation with running water for a day; the NH_4OH for dissolving the silver oxide was prepared from gaseous ammonia. The reaction with the ketone in the absence of alkali proceeded less vigorously and this could be observed as a

slower blackening of the solution than that seen in the presence of alkali. Experiments at a raised temperature were carried out at 40 and 52° in the presence and the absence of alkali. At a raised temperature the alkali also accelerated the reaction as at room temperature. The products of reaction at 40° were investigated as described previously [1]: from 0.28 g of ketone, we obtained 0.2 g of neutral, semiliquid product, which had the same character as that obtained from the room temperature reaction. The solutions left after extraction of the neutral products were collected from several experiments: after evaporating down and acidifying, no acidic products at all could be found. Separate experiments were carried out with the addition of ethyl alcohol to dissolve the ketone before the oxidizing solution was added. Data presented in the table show that the consumption of Ag_2O in this case, as also on changing other experimental conditions, remained constant.

Investigation of the ketoalcohol phenylacetylcarbinol. The phenylacetylcarbinol was prepared from bromobenzyl methyl ketone by treatment with potassium formate in methanol solution [5]. After fractionation in vacuum from 15.8 g of impure bromoketone we obtained 4.0 g of a ketoalcohol with b.p. 129-131° at 14 mm, n_D^{20} 1.5313 (according to literature data: b.p. 121-122° at 11.5 mm, n_d^{16} 1.5313 [6]). The ketoalcohol was used in the freshly prepared form. The reaction of the ketoalcohol with Ag_2O was carried out under the same conditions as those used to investigate the reaction with ketones, in most cases at room temperature and in other cases with heating to 40° at the end of the experiment. The ketoalcohol reacted very readily with Ag_2O, from external appearances more vigorously than the ketones. The reaction products were investigated as described above: from 0.72 g of ketoalcohol we obtained 0.35 g of benzoic acid, m.p. 122-122.5°, after recrystallization from water, undepressed by authentic benzoic acid; the formation of acetic acid was demonstrated qualitatively (by the formation of ethyl acetate and basic iron salt); a qualitative reaction for formic acid was negative. In addition we obtained 0.07 g of a tarry, neutral substance. The consumption of Ag_2O under different experimental conditions is shown in the table.

SUMMARY

1. We investigated the reaction of an ammonia solution of silver oxide with dibenzyl ketone.

2. It was shown that the consumption of silver oxide in the reaction with methyl benzyl ketone was constant, irrespective of the presence or absence of alkali in the reaction mixture or of temperature (from room to 40-50°).

3. It was shown that the reaction of ketones with an ammonia solution of silver oxide did not proceed through a stage of ketoalcohol formation.

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β-AMINOVINYL KETONES

VIII. THE SYNTHESIS OF ALKYL β-ALKYLAMINOVINYL KETONES

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β-Aminovinyl ketones of various types are readily prepared by reacting β-chlorovinyl ketones with ammonia and amines. Up to now this reaction has been known for ketovinylation of ammonia [1], secondary amines [2] and tertiary amines [3], which gives β-aminovinyl ketones, β-dialkylaminovinyl ketones and quaternary salts of β-ketovinyl ammonia, respectively. In this short report we give data on the ketovinylation of primary aliphatic amines that resulted in the formation of β-alkylaminovinyl ketones.

$$RCOCH{=}CHCl + NH_2R' \rightarrow RCOCH{=}CHNHR'$$

$R = CH_3$, n-C_3H_7, iso-C_4H_9; $R' = CH_3$, C_2H_5

As in the case of ketovinylation of ammonia and secondary amines, the reaction of β-chlorovinyl ketones with primary amines was carried out in an aqueous solution, and in this case, a large excess and high concentration of amine was not necessary. To obtain high yields of β-alkylaminovinyl ketones (70-90%), a 2.5-4 fold excess of amine used in the form of 5-10% aqueous solution, was sufficient. The reaction is best carried out at a temperature of about 5° with very vigorous stirring. Using this method, we obtained 5 examples of the little known class of alkyl β-alkylaminovinyl ketones, whose sole method of preparation had previously been one based on the treatment of hydroxymethylene ketones with primary amines [4]. The method proposed by us is more convenient due to the accessibility of the starting β-chlorovinyl ketones and the complete unambiguity of their structure as well as the simplicity of the procedure, high yields and absence of any side processes.

Alkyl β-alkylaminovinyl ketones are colorless, oily liquids that gradually become yellow. They boil at about 15° lower than the corresponding alkyl β-aminovinyl ketones $RCOCH{=}CHNH_2$, which are unsubstituted at the nitrogen and equal to them in molecular weight. From this one can conclude that they have a somewhat lower polarity, which is also confirmed by the data on their solubility: most of the alkyl β-alkylaminovinyl ketones dissolve in water with difficulty and readily in nonpolar solvents. The refractive index of alkyl β-alkylaminovinyl ketones does not change with time, as occurs with alkyl β-aminovinyl ketones [1, 5].

EXPERIMENTAL

Over a period of 20-30 minutes, 0.5 mole of alkyl β-chlorovinyl ketone was added to a cooled solution of 1.5-2 moles of methylamine or ethylamine in 600 ml of water, while the temperature of the reaction mixture was kept at about 5°. The mixture was stirred for a further 1 hour, saturated with potash and extracted with ether in a liquid extractor for 5-6 hours. The extract was dried over potash, the ether distilled off and the residue distilled in vacuum. The yields, constants and analyses of the substances obtained by this method are presented in the table.

Formula	Yield (in %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		EMR_D	% C		% H	
					found	calc.		found	calc.	found	calc.
$CH_3COCH=CHNHCH_3$*	72	77—78 (13)	1.5687	0.9851	32.96	28.33	4.63	60.31, 60.37	60.59	9.38, 9.31	9.15
$CH_3COCH=CHNHC_2H_5$	78	63—64 (4)	1.5427	0.9543	37.36	33.05	4.31	63.54, 63.32	63.69	9.82, 9.80	9.94
$n\text{-}C_3H_7COCH=CHNHC_2H_5$	81	70 (3)	1.5223	0.9228	46.70	42.29	4.41	68.11, 68.07	68.05	10.91, 10.80	10.71
$n\text{-}C_4H_9COCH=CHNHCH_3$	91	73—74 (4)	1.5243	0.9292	46.51	42.29	4.22	67.97	68.05	10.71	10.71
$n\text{-}C_4H_9COCH=CHNHC_2H_5$	85	76 (4)	1.5140	0.9105	51.34	46.90	4.44	69.79	69.64	11.14	11.04

* Literature data: b.p. 90-93°(17 mm) [4], $n_C^{22.4}$ 1.53617, $d_4^{22.4}$ 0.9869 [6]. According to our data, which differ from the above, the substance described by Auwers [6] was not quite pure.

SUMMARY

A general method was developed for the synthesis of alkyl β-alkylaminovinyl ketones by reacting alkyl β-chlorovinyl ketones with primary amines to give 70-90% yields.

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CATALYTIC CONDENSATION OF ACETYLENE WITH AROMATIC AMINES

XXVII. CATALYTIC SYNTHESIS OF 3-PHENYL-BENZO[F]QUINOLINE DERIVATIVES

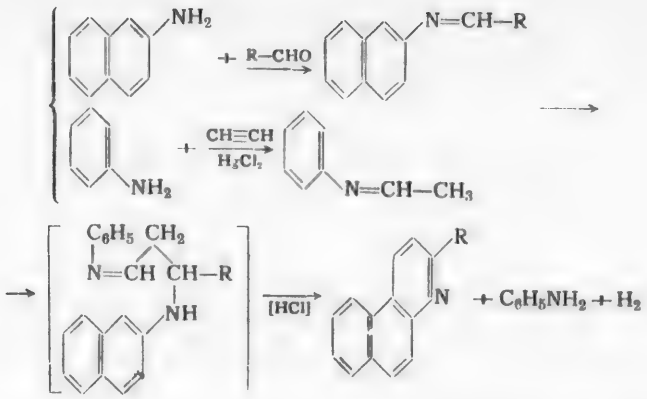
N. S. Kozlov and O. K. Kozminykh

The synthesis of phenyl derivatives of benzo[f]quinoline has hardly been investigated and very few compounds of this series have been synthesized. Thus, for example, derivatives of 3-phenyl-benzo[f]quinoline with a substituent in the phenyl radical were prepared by Doebner's method [1, 7], from 2-naphthylamine, an aromatic aldehyde and pyrotartaric acid in two stages: first the derivatives of 3-phenyl-benzo[f]quinoline-1-carboxylic acid were synthesized and then decarboxylated by heating, to the corresponding phenylbenzoquinoline.

Considering this phenomenon, we decided to use a reaction, investigated by one of us [2-5], namely catalytic condensation of acetylene with aromatic amines and aldehydes, for the synthesis of 3-phenyl-benzo[f]-quinoline derivatives. For this purpose we reacted acetylene with 2-naphthylamine and various aromatic aldehydes, namely: benzaldehyde, anisaldehyde, p-dimethylaminobenzaldehyde, piperonal, salicylaldehyde and, finally, m-nitrobenzaldehyde. As a result of the experiments, we were able to synthesize in good yields 3-phenyl-benzo[f]quinoline and its derivatives with substituents in the phenyl radical, namely: 3-(4'-methoxyphenyl)-benzo[f]quinoline, 3-piperonyl-benzo[f]quinoline, 3-(4'-dimethylaminophenyl)-benzo[f]quinoline, 3-(2'-hydroxyphenyl)-benzo[f]quinoline and 3-(3'-nitrophenyl)-benzo[f]quinoline.

In this work we suceeded in considerably improving the method we proposed previously [2-4] for the synthesis of phenyl derivatives of quinoline, starting with acetylene, aromatic amines and aromatic aldehydes. As is known, basically the method consists of saturating with acetylene a mixture of the primary aromatic amine and the aromatic aldehyde in molecular ratios of 2:1 in the presence of a catalyst. According to our understanding of the reaction mechanism, half of the aromatic amine reacts with the aromatic aldehyde and forms the corresponding Schiff's base, the other half of the same aromatic amine reacts with acetylene, forming the corresponding monoethylidene base. Then the bases obtained react with each other forming an intermediate product, which after cylization is converted into a phenyl derivative of quinoline. Consequently, the course of the reaction depends on the capacity of the aromatic amine to react with the aromatic aldehyde, though mainly, with acetylene, and on the capacity of the intermediate product to cyclize. We found that in carrying out these syntheses in practice, not all aromatic amines had the same degree of reactivity with acetylene. Aniline was found to be the most reactive among them.

At the same time, we presumed that the monoethylidene aniline base should react most vigorously with the corresponding Schiff's base, while the intermediate product formed should have a high capacity to cyclize into a quinoline base. Therefore, we decided to synthesize phenylquinoline bases by a method different from the previous one, namely, having prepared a suitable Schiff's base from some aromatic aldehyde and an aromatic amine, we added to it an equimolecular amount of aniline and the reaction mixture thus obtained was saturated with acetylene in the presence of a catalyst. Previously, the cyclization of the intermediate product was accomplished by a thermal method and the condensation product distilled, but in the case of compounds of high molecular weight, distillation was not always possible. Therefore, we carried out the cyclization by heating the condensation product with hydrochloric acid, in a 10% aqueous-alcohol solution. Hydrochloric acid was found to be a good cyclization catalyst. The substitution of aniline for half the quantity of aromatic amine made the synthesis of phenylquinoline compounds even simpler and confirmed our formed ideas on their synthesis mechanism. Hence, the synthesis of 3-phenyl-benzo[f]quinolines have the following mechanism:



Thus, this work has widened the application of acetylene condensation with aromatic amines and aromatic aldehydes and, at the same time, allowed the development of a new, simpler and better method for synthesizing 3-phenyl-benzo[f]quinoline derivatives.

EXPERIMENTAL

Experiments on the catalytic condensation of 2-naphthylamine with aromatic aldehydes and acetylene were carried out by the following method. First, the Schiff's base was obtained as a crystalline product from 2-naphthylamine and the aromatic aldehyde, dissolved in methyl alcohol, by heating on a water bath. Then the Schiff's base was dissolved in toluene, mixed with an equimolecular amount of aniline and the reaction mixture saturated with acetylene in the presence of mercuric chloride, while heating on a water bath to 70-80°. The absorption of acetylene proceeded most actively in the first 2-3 hours of the experiment. After complete saturation of the reaction mixture with acetylene, which took about 15 hours, at 10% aqueous alcohol solution of HCl was added to the reaction product and the mixture heated for 1 hour on a water bath. Under these conditions cyclization of the intermediate occurred with the formation of the hydrochloride of a benzo[f]quinoline, which readily and almost quantitatively separated as crystals on further cooling the mixture. The hydrochloride was purified by recrystallization and converted into the free base by treatment with ammonia. In some cases the hydrochloride of the product was not isolated and by neutralizing the hydrochloric acid solution with ammonia the free base was precipitated in an amorphous or crystalline form and then purified by recrystallization from acetone and pyridine.

During the reaction process, the catalyst – mercuric chloride – formed an organic complex or a salt of unknown composition, which was separated from the reaction mixture after treating the mother solution of hydrochloride with ammonia. At the end of the reaction, part of the catalyst was converted into a grey precipitate of finely dispersed mercury.

Synthesis of 3-phenyl-benzo[f]quinoline. From 15 g of 2-naphthylamine and 11.1 g of benzaldehyde, we obtained a Schiff's base with m.p. 106°. The Schiff's base was dissolved in toluene, mixed with 8.5 g of aniline and 4 g of mercuric chloride and saturated with acetylene. At the end of the reaction course yellow crystals formed in the flask on a thin layer of tar. The crystals were separated mechanically, washed free from tar with methyl alcohol and recrystallized toluene or acetone. The yield of pure product was 6.8 g (61.3%, calculated on aldehyde). The m.p. was 188°. The picrate had m.p. 250°. The constants of this product corresponded to the literature data [6] for 3-phenyl-benzo[f]quinoline.

Synthesis of 3-(4'methoxyphenyl-benzo[f]quinoline. From 15 g of 2-naphthylamine and 14.2 g of anisaldehyde we obtained a Schiff's base with m.p. 102-103°. To a toluene solution of the Schiff's base was added 10 g of aniline and 5 g of mercuric chloride and the mixture saturated with acetylene. At the end of the reaction a voluminous yellow precipitate separated, which was heated in 10% aqueous alcoholic hydrochloric acid and white

crystals of the free base precipitated from the solution with ammonia. The weight of the product was 6.5 g (46.4%). The product crystallized from acetone and pyridine as lustrous, white plates with m.p. 192-192.5°.

Found %: C 84.33, 84.41; H 5.05, 5.31; N 4.93, 5.15. $C_{20}H_{15}ON$. Calculated %: C 84.18; H 5.29; N 4.90.

Synthesis of 3-(4'-dimethylaminophenyl-benzo[f]quinoline. From 15 g of 2-naphthylamine and 15.6 g of p-dimethylaminobenzaldehyde we obtained a Schiff's base with m.p. 165-166°. To the Schiff's base in toluene was added 10 g of aniline and 5 g of mercuric chloride and the mixture saturated with acetylene. At the end of the reaction, a 10% aqueous alcohol solution of HCl was added, the mixture heated and the free base precipitated with ammonia. The yield of product was 12.8 g (82%). The product was crystallized from acetone and pyridine as thin yellow-green needles with m.p. 237-238°.

Found %: C 84.26, 84.49; H 5.99, 5.81; N 9.66, 9.35. $C_{21}H_{16}N_2$. Calculated %: C 84.52; H 6.08, N 9.38.

Synthesis of 3-piperonyl-benzo[f]quinoline. From 15 g of 2-naphthylamine and 15.7 g of piperonal (heliotropin) we obtained a Schiff's base with m.p. 119-120°. To a toluene solution of the Schiff's base was added 11 g of aniline and 5 g of mercuric chloride and the mixture saturated with acetylene. It was worked up as described above. The yield was 9 g (57.3%). The product crystallized from pyridine as thin, white plates with m.p. 178.5-179°. The picrate had m.p. 253° (decomp.).

Found %: C 80.40, 80.17; H 4.54, 4.63; N 4.58, 4.43. $C_{20}H_{13}O_2N$. Calculated %: C 80.25; H 4.37; N 4.68.

Synthesis of 3-(2'-hydroxyphenyl)-benzo[f]quinoline. From 15 g of 2-naphthylamine and 12.8 g of salicyaldehyde we obtained a Schiff's base with m.p. 128.5°. To a solution of the Schiff's base in toluene was added 10 g of aniline and 5 g of mercuric chloride and the mixture saturated with acetylene. The base formed orange crystals, which were recrystallized from pyridine, m.p. 218°. The yield was 6.8 g (53.1%).

Found %: C 83.96, 84.24; H 4.63, 4.73; N 4.89, 4.99. $C_{19}H_{13}ON$. Calculated %: C 84.10, H 4.83; N 5.16.

Synthesis of 3-(3'-nitrophenyl)-benzo[f]quinoline. From 15 g of 2-naphthylamine and 16 g of m-nitrobenzaldehyde we obtained a Schiff's base with m.p. 96°. A toluene solution of the Schiff's base was mixed with 10 g of aniline and 5 g of mercuric chloride and saturated with acetylene. After the reaction the mixture was heated in 10% aqueous alcoholic hydrochloric acid and after cooling, crystals of the hydrochloride separated, which were treated with ammonia in alcohol solution to deposit pale yellow, thin needles of the base with m.p. 182-183° (from pyridine). The yield was 9 g (55.5%).

Found %: C 75.87, 76.13; H 4.18; N 9.29, 9.50. $C_{19}H_{12}O_2N_2$. Calculated %: 75.98; H 4.02, N 9.32.

SUMMARY

1. A new method has been developed for the synthesis of 3-phenyl-benzo[f]quinoline derivatives by the catalytic condensation of 2-naphthylamine and a series of aromatic aldehydes with acetylene.

2. We synthesized 6 compounds of this series.

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SPECTROPHOTOMETRIC INVESTIGATION OF DIPHENYLAMINE AND ITS DERIVATIVES IN CONCENTRATED SULFURIC ACID. I.

P. M. Bugai

1. Diphenylamine absorption spectra. While investigating various diphenylamine derivatives in concentrated sulfuric acid, we noticed that the color deepened and became more intense when these solutions were stored for a long time in closed flasks. This phenomenon encouraged us to investigate the mechanism and kinetics of the reaction of diphenylamine and some of its derivatives with concentrated sulfuric acid, under prolonged treatment with the latter. The investigations were carried out on an SF-4 spectrophotometer.

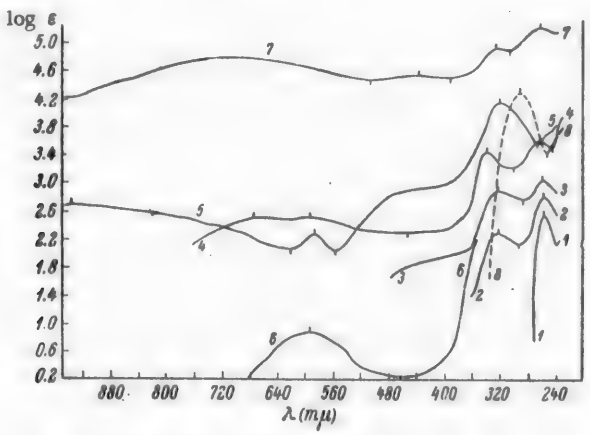


Fig. 1. Diphenylamine absorption spectra.
1) At the moment of dissolving in H_2SO_4 ($1 \cdot 10^{-3}$ M), 2) 19 days after dissolving in H_2SO_4 ($1 \cdot 10^{-3}$ M), 3) 28 days after dissolving in H_2SO_4 ($1 \cdot 10^{-3}$ M), 4) the solution in H_2SO_4 was heated on a water bath for 60 hours, precipitated with water and plotted in concentrated sulfuric acid ($1 \cdot 10^{-4}$ M), 5) the preceding solution was diluted 10-fold with water ($1 \cdot 10^{-3}$ M), 6) solution in H_2SO_4 stood for 265 days in the cold, precipitated with water and spectrum plotted in ethanol ($1 \cdot 10^{-3}$ M), 7) diphenylamine was oxidized with hydrogen peroxide, percipitated with water and spectrum plotted in a solution of concentrated sulfuric acid ($1 \cdot 10^{-5}$ M), 8) spectrum of diphenylamine hydrochloride plotted in an ethanol solution ($1 \cdot 10^{-4}$ M).

Diphenylamine and its derivatives were purified to spectrographic purity, while the sulfuric acid was used after distillation. Figure 1 shows the absorption spectrum curves of sulfuric acid solutions of diphenylamine, obtained after different periods of storage. Curve 1 shows an absorption spectrum of diphenylamine at the moment of dissolving in sulfuric acid. Other authors [1, 2] have also plotted the spectrum of diphenylamine

TABLE 1

Curve no. in Fig. 1	Concen. substance when spectrum plotted (M)	No. of days after sol. spectrum plotted	Color of solution in conc. H_2SO_4	Band order	Absorption band maxima		Increase in absorption intensity of band maxima over the first value
					ε	λ (mμ)	
1	$1 \cdot 10^{-3}$	At the moment of dissolving in H_2SO_4	Colorless	I	346.7	254	1.0
2	$1 \cdot 10^{-3}$	19	Same	I	616.6	254	1.8
				II	190.5	320	1.0
3	$1 \cdot 10^{-3}$	28	Slightly blue	I	1072	254	3.1
				II	758.6	318	4.0
				III	100—158	370—352	1.0
4 *	$1 \cdot 10^{-4}$	Heated for 60 hours	Light greenish blue	I	3802	256	10.9
				II	2692	335	14.0
				III a	316	590	1.0
				IV	316	670	1.0
5 **	$1 \cdot 10^{-3}$	—	Light green	II	13490	316	71.0
				III	676—1413	470—370	8.0
				III a	182	585	0.6
				IV	490	935	1.6
6 ***	$1 \cdot 10^{-2}$	265	Light blue	IIIa	7.6	590	0.02
				—	1.7	464 (min)	—
7 ****	$1 \cdot 10^{-5}$	—	Bluish green	I	162200	255	470.0
				II	83180	320	438.0
				III	33880	435	271.0
				IV	57540	700	182.0
8	$1 \cdot 10^{-4}$	At the moment of dissolving in ethanol	—	I	19950	286	57.5

* The sulfuric solution of diphenylamine was heated on a water bath for 60 hours, precipitated with water and the spectrum plotted in concentrated sulfuric acid.

** The colored sulfuric acid solution of diphenylamine, after heating on a water bath for 60 hours, was diluted 10-fold with water and the spectrum of this solution was plotted.

*** The diphenylamine in sulfuric acid was kept for 265 days in the cold, precipitated with water and the spectrum plotted in ethanol.

**** Diphenylamine was oxidized with hydrogen peroxide in an acidic medium, precipitated and the spectrum plotted in concentrated sulfuric acid solution.

sulfate. The appearance of the curve and its absorption bands in the ultraviolet region is characteristic of diphenylamine sulfate (Fig. 1).

Then a spectrum of the solution was plotted after 19 days (Curve 2). Curve 2 has a considerably higher absorption intensity than Curve 1 and forms a new band with an absorption maximum. The first band of Curve 2, on the ultraviolet side, coincides in wavelength with the similar maximum of Curve 1, but has a higher absorption intensity. A new band with an absorption maximum at 320 mμ was formed as a result of prolonged treatment of diphenylamine with concentrated sulfuric acid.

Curve 3 in Fig. 1 represents the absorption spectrum of a sulfuric acid solution of diphenylamine obtained 28 days after the diphenylamine was dissolved. This curve has a considerably higher absorption intensity than Curves 1 and 2 and is different in character and position.

We heated a sulfuric acid solution of diphenenylamine for 60 hours on a water bath to accelerate the reaction of diphenylamine with concentrated sulfuric acid. Curve 4, Fig. 1, gives its absorption spectrum. This curve copies 3 to a considerable extent in the ultraviolet region, and then extends far into the visible region,

forming new bands with absorption maxima. Curve 4 has a considerably higher absorption intensity than the preceding curve. The maximum of the first absorption band practically coincides with the similar maxima of Curves 3 and 2. The maximum of the second absorption band (335 mμ) is displaced by 15-17 mμ further into the long wavelength region than the corresponding maxima of Curves 3 and 2. In the visible region the curve forms two weak bands with absorption maxima at 590 and 670 mμ.

In addition, the degree of stability of the colored material, obtained from diphenylamine by prolonged treatment with concentrated sulfuric acid, was a problem that interested us. For this reason the colored sulfuric acid solution, obtained after heating for 60 hours on a water bath, was diluted ten-fold with water and the spectrum plotted. Curve 5 illustrates the character of the spectrum of this aqueous sulfuric acid solution. In Curve 5 the band with an absorption maxima at 316 mμ almost coincides with the similar bands of Curves 3 and 2. On the ultraviolet side the band's minimum coincides with the maxima of the first absorption bands of all the preceding curves. The changes in absorption intensity of the corresponding maxima are illustrated by numerical data in Table 1.

The position of Curve 5 and the formation of characteristic bands for the colored solution indicate that we were dealing not with pure diphenylamine, but with a new product which had been formed from diphenylamine by prolonged treatment with concentrated sulfuric acid. Consequently, the water had not hydrolyzed this colored substance.

Then we kept the solution of diphenylamine in sulfuric acid in a closed flask for 265 days. After such prolonged storage, the solution became bluish green. Its spectrum in the visible region is represented by Curve 6, Fig. 1. This curve forms a wide band with an absorption maximum and a minimum at 590 and 464 mμ, at a very low absorption intensity (Fig. 1, and Table 1).

To confirm the presence of oxidation products of diphenylamine from prolonged treatment with concentrated sulfuric acid using the absorption spectra, we oxidized diphenylamine with hydrogen peroxide in an acidic medium, separated the colored product with water and then prepared a sulfuric acid solution of it and plotted its absorption spectrum. This absorption spectrum is expressed by Curve 7, Fig. 1. (The sample was calculated for the oxidized product – diphenylbenzidine).

In the ultraviolet region Curve 7 has two absorption bands whose maxima coincide with the corresponding maxima of Curves 3 and 2 and the maximum of the first absorption band coincides with the similar maximum of Curve 4. Further on, Curve 7 extends far into the visible region, forming new absorption bands, – one with a weakly expressed maximum at 435 mμ and a second, wider band with an absorption maximum at 700 mμ. The maxima of the first and second bands of Curve 7 are tens and hundreds of times greater in absorption intensity than the similar maxima of the preceding curves.

Consequently, we have here a complete analogy with the curves obtained by reacting diphenylamine with concentrated sulfuric acid.

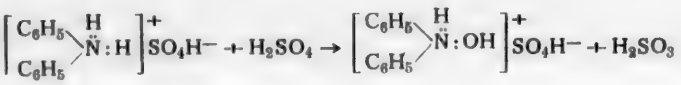
The experiments we carried out on the oxidation of diphenylamine with concentrated sulfuric acid in an atmosphere of oxygen and an atmosphere of nitrogen, show that oxidation occurred in both cases, as identical absorption bands were observed, although the intensity of the absorption bands, formed in the presence of oxygen, was somewhat greater than when the reaction occurred in an atmosphere of nitrogen.

In order to find out how a freshly-prepared diphenylamine salt would be hydrolyzed, we prepared diphenylamine hydrochloride (by passing dry hydrogen chloride through a benzene solution of diphenylamine). Curve 8 in Fig. 1 represents the absorption spectrum of an ethanol solution of this salt. This curve differs sharply from all the curves found for sulfuric acid solutions. It has one band with an absorption maximum at 286 mμ and its absorption intensity is high in comparison with the maxima of Curves 5, 3 and 2, in the ultraviolet region. The location and absorption maximum of Curve 8 almost completely duplicates the curve of diphenylamine in an ethanol solution. Thus, the diphenylamine salt was completely hydrolyzed when dissolved in ethanol.

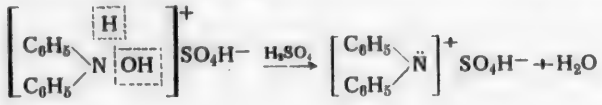
Passing on to the problem of the mechanism of the chemical reaction of concentrated sulfuric acid with diphenylamine and using certain literature data, we propose the following reaction scheme

$$C_6H_5-\underset{\underset{H}{|}}{\ddot{N}}-C_6H_5 + H_2SO_4 \rightarrow \left[C_6H_5-\overset{H}{\underset{|}{\ddot{N}}}-C_6H_5 \right]^+ SO_4H^-$$

Then, concentrated sulfuric acid oxidizes the diphenylammonium ion

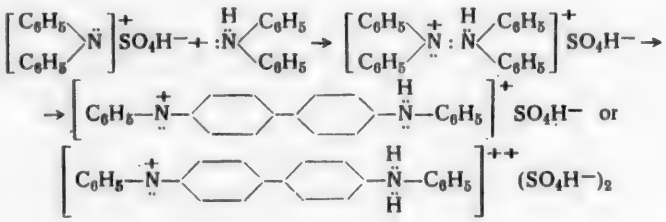


After that, under the effect of sulfuric acid, the diphenylhydroxylammonium ion is dehydrated

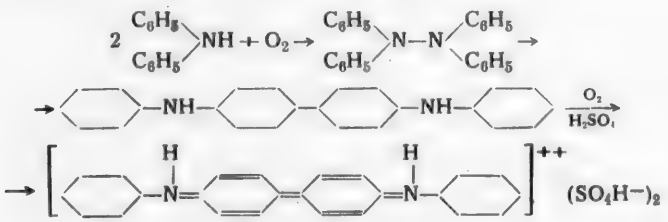


(the ion is bluish green in color)

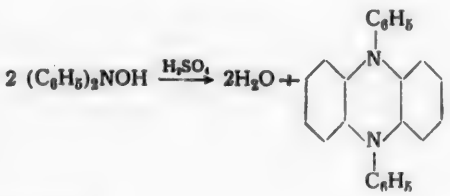
We had carried out a similar reaction previously [3]. V. Khyukkel [4] mentions a similar process of sulfate formation followed by dehydration in his book. Then during the oxidation, condensation and benzidine rearrangement occur with subsequent formation of an azenium salt of a benzidine derivative.



Data from the work of F. Kehrmann and St. Micewicz [5] on diphenylamine oxidation with oxidants in an acidic medium may be given as confirmation of an analogous condensation



and H. Wieland [6], who, without rejecting the possibility of a Kehrmann-Micewicz reaction, considered that in diphenylamine oxidation, condensation occurred with the formation of a phenazine salt, and he used as proof the fact that phenazine was also formed by treating diphenylhydroxylamine with concentrated sulfuric acid



and then phenazine sulfate was formed.

Thus, we consider that on oxidizing diphenylamine with concentrated sulfuric acid, first diphenylhydroxylamine and its sulfate are formed as intermediate products, and then by dehydration, the azenium ion – the color carrier of the material – is formed. Then this ion condenses with diphenylamine and forms the colored molecules of a diphenylbenzidine azenium salt.

V. S. Smirnov [7] also studied the oxidation of diphenyl- and triphenylamines, but he was not interested in the reasons and chemistry of the formation of colored substances, as we are.

2. Absorption spectra of 4-hydroxydiphenylamine. 4-Hydroxydiphenylamine was synthesized by a method we developed [8] and 4-methoxydiphenylamine was prepared by methylating the first substance. The constants of both substances corresponded to literature data. The substances were purified to spectrographic purity.

In Fig. 2, curve 1 represents the absorption spectrum of a solution of 4-hydroxydiphenylamine in concentrated sulfuric acid, plotted at the moment of dissolving. This curve has one band with an absorption maximum at 285 mμ. We have given the absorption spectrum curve of 4-hydroxydiphenylamine in an ethanol solution for comparison. This is curve 6 in Fig. 2. We see that it has one small band with an absorption maximum at 244 mμ, which coincides with the minimum of curve 1. The second band of the ethanol solution has an absorption maximum that is displaced by 5 mμ into the short wavelength region from the analogous maximum of curve 1 and has a somewhat lower absorption intensity.

After 6 days we plotted the spectrum of the sulfuric acid solution. This solution remained colorless and curve 2 which was obtained differs little from curve 1. The maxima of the absorption bands in curve 2 have the same wavelength but the absorption maximum intensity of curve 2 is higher than that of curve 1.

A noticeable change in absorption spectra occurred 12 days after solution in acid; curve 3 shows this difference. The solution became slightly greenish. However, in the ultraviolet the position of the maximum of this curve's 1st absorption band was identical with the positions of the maxima of the absorption bands of curves 1 and 2; besides that, a new band in the form of an inflexion was formed in the curve at 305-322 mμ. Then curve 3 extended into the far visible region and formed a series of absorption bands in the form of inflexions in the curve and with band maxima at 540 and 700 mμ.

Curve 4 represents the absorption spectrum of a sulfuric acid solution of 4-hydroxydiphenylamine which was plotted 30 days after the preparation of the solution. Curve 4 has a higher absorption intensity than the preceding curves and has a different character. Thus, on the ultra-violet side, the curve has a inflexion in the form of a step. The maximum of the first band has the same position as the maxima of the preceding curves but it has a somewhat higher absorption intensity (Table 2).

A new band appears in curve 4 with an absorption maximum at 320 mμ instead of the step of the preceding curve and has an absorption intensity 3.5 times greater than that of the step. Then this curve again forms a sharp inflexion at 370-344 mμ and continues into the far visible region almost parallel to curve 3, forming other absorption bands (curve 4, Table 2).

Curve 5 of the absorption spectra was obtained 45 days after 4-hydroxydiphenylamine was dissolved in concentrated sulfuric acid. This curve is similar to curve 4, but has a somewhat higher absorption intensity; the solution became a light reddish violet color.

On the ultraviolet side, a small band is formed with an absorption maximum at 256 mμ and is denoted as band Ia in Table 2. The maximum of the 1st absorption band has a wavelength that coincides with those of the band maxima of the preceding curves, but it has a somewhat higher absorption intensity (curve 5, Table 2). The wavelength of the band II maximum coincides with the position of the inflexion in curve 3 and with the maximum of band II of curve 4, but it has a somewhat higher absorption intensity.

Then curve 5 also forms an inflexion, the same as curve 4, and continues almost parallel to curve 4 in the visible region, forming an analogous band with an absorption maximum at 660 mμ.

One may conclude that 4-hydroxydiphenylamine with concentrated sulfuric acid formed as insignificant amount of sulfate, which may be seen by comparing curves 1 and 6, i.e., 4-hydroxydiphenylamine, plotted at the moment of dissolving in acid and in an ethanol solution.

TABLE 2

Curve no. in Fig. 2	Days after sol. spectrum plotted	Color of solution in conc. H_2SO_4	Band order	Absorption band maxima		Increase in absorption intensity band maxima over the 1st value
				ε	λ (mμ)	
1	At the moment of dissolving in H_2SO_4	Colorless	I	18200	285	1.0
2	6	Colorless	I	22390	285	1.23
3	12	Greenish	I	23440	285	1.3
			II	2512—3981	332—305	1.0
			III	398—501	390—356	1.0
			IV	398	540	1.0
			V	631	700	1.0
4	30	Light green	I a	15850	265—257	1.0
			I	25700	285	1.4
			II	10720	320	3.5
			III	1995—3162	370—344	5.6
			V	1778	660	2.8
5	45	Reddish violet	I a	23440	256	1.5
			I	29510	285	1.6
			II	19050	320	5.9
			III	3802—5623	370—344	10.4
			V	3981	660	6.3
6	At the moment of dissolving in ethanol	—	I a	6166	244	0.4
			I	15850	280	0.87

Note: The concentration of the substance when the spectra were plotted was $5 \cdot 10^{-5}$ m.

The constancy of wavelengths of the absorption maxima at 285 mμ of all the curves investigated and the insignificant increase in absorption intensity of this band also confirm the weak salt formation of 4-hydroxydiphenylamine, in which the hydroxyl group in the para-position greatly affects this capacity of the molecule.

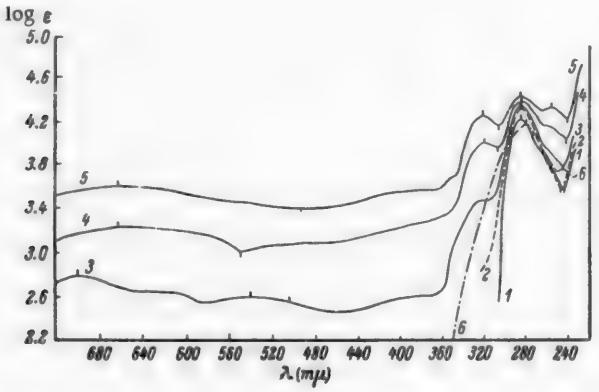
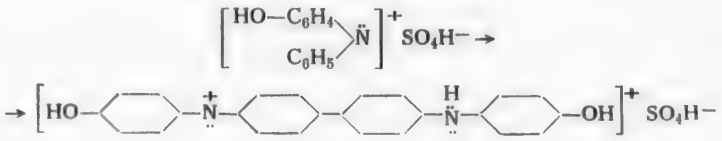


Fig. 2. Absorption spectra of 4-hydroxydiphenylamine ($5 \cdot 10^{-5}$ M concentration).
1) At the moment of dissolving in H_2SO_4, 2) 6 days after dissolving in H_2SO_4, 3) 12 days after dissolving in H_2SO_4, 4) 30 days after dissolving in H_2SO_4, 5) 45 days after dissolving in H_2SO_4, 6) at the moment of dissolving in ethanol.

The formation of band II with an absorption maximum in the region of 320 mμ, and then the appearance of an absorption band in the whole visible region when colored solutions are formed indicates that here a chemical reaction occurs between 4-hydroxydiphenylamine and concentrated sulfuric acid, with sulfuric acid as the oxidant, medium and salt former, similar to that observed in the oxidation of diphenylamine with sulfuric acid.

One of the intermediate products was an azenium salt which then condensed with 4-hydroxydiphenylamine and was converted into an azenium salt of dihydroxydiphenylbenzidine



or formed a dibasic salt with two molecule of sulfuric acid.

The benzidine type of compounds mentioned above have an intense color.

We consider that the spectrophotometric data we obtained for 4-hydroxydiphenylamine in a solution of concentrated sulfuric acid also indicate deep chemical conversions of the material when treated with sulfuric acid. This is also indicated by the fact that the solution changed from a colorless one to a deeply colored one and with a 10-fold and more dilution, its color hardly changed.

3. Absorption spectra of 4-methoxydiphenylamine. Curve 1 in Fig. 3 represents the absorption spectrum of a sulfuric acid solution of 4-methoxydiphenylamine, obtained at the moment of dissolving in the acid. This curve has one band with an absorption maximum at 265 mμ. The character of curve 1 indicates that this substance forms a sulfate readily, i.e., behaves similarly to diphenylamine, which, as stated above, also has one band with an absorption maximum, but with a lower absorption intensity.

TABLE 3

Curve no. in Fig. 3	Concent. substance when spectrum plotted (M)	Days after sol. spectrum plotted	Color of solution in conc. H_2SO_4	Band order	Absorption band maxima		Increase in absorption intensity of band maxima over the first value
					ε	γ (mμ)	
1	$1 \cdot 10^{-3}$	At moment of dissolving	Colorless	I	525	265	1.0
2	$1 \cdot 10^{-3}$	5	The same	I	1122	285	2.1
				II	62	322	1.0
3	$1 \cdot 10^{-3}$	13	Pinkish	I	2089	283	4.0
				II	77.6	328	1.3
				III	13	430	1.0
				IV	10	700	1.0
4	$1 \cdot 10^{-4}$	25	Light lilac	I	3162	285	6.0
				II	1259	317	20.3
				III a	309	370	1.0
				III	204	600	15.7
				IV	195	710	19.5
5	$5 \cdot 10^{-5}$	At moment of dissolving in ethanol	—	I a	6918	241	1.0
				I	21880	284	41.3

Even after 5 days the sulfuric acid solution of 4-methoxydiphenylamine changed considerably in comparison with the initial state, as is shown graphically by curve 2 in Fig. 3. This curve, which shows a considerable increase

in absorption intensity, is displaced into the long wavelength region and forms two more bands with absorption maxima (curve 2, Fig. 3, Table 3).

Curve 3 was obtained after 13 days. In this case the sulfuric acid solution was already pink. Curve 3, like curve 2, has two bands with absorption maxima in the ultraviolet region, approximately in the same wavelength region, but, besides that, it has two additional bands with absorption maxima in the visible region (Fig. 3, curve 3 and Table 3).

Curve 4, which was obtained 25 days after the material was dissolved in sulfuric acid, shows an even sharper change in the character of the absorption spectrum. The absorption intensity increases sharply and the maximum of the second band is displaced into the short wavelength region in comparison with the similar maxima on curves 2 and 3. Further on, curve 4 forms band III with an absorption maximum at 370 mμ, at the small inflexion, which curve 3 had in this region. Then in the far visible region the curve forms two bands with absorption maxima at 600 and 700 mμ.

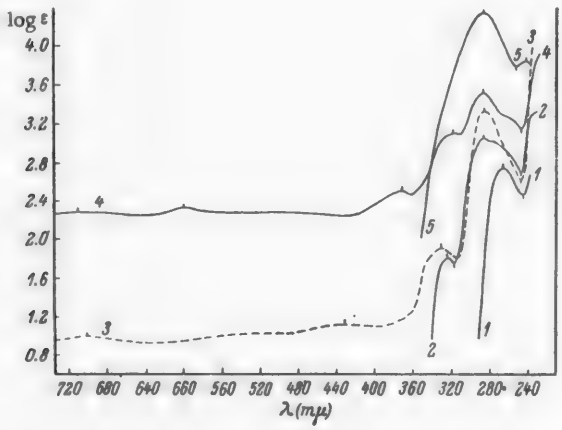


Fig. 3. Absorption spectra of 4-methoxydiphenylamine. 1) At the moment of dissolving in H_2SO_4 ($1 \cdot 10^{-3}$ M), 2) 5 days after dissolving in H_2SO_4 ($1 \cdot 10^{-3}$ M), 3) 13 days after dissolving in H_2SO_4 ($1 \cdot 10^{-3}$ M), 4) 25 days after dissolving in H_2SO_4 ($1 \cdot 10^{-4}$ M), 5) at the moment of dissolving in ethanol ($5 \cdot 10^{-5}$ M).

The curve of the absorption spectrum of 4-methoxydiphenylamine in an ethanol solution is given for comparison with the absorption spectra of sulfuric acid solutions. On the ultraviolet side curve 5 forms a small band Ia with an absorption maximum at 241 mμ, while the maximum of the absorption band I is close in wavelength to the maxima of the first bands of curves 2 and 4 and coincides with the maximum in curve 3.

As the bands with absorption maxima of sulfuric acid solutions (the first absorption bands), which had stood for a long time (but not at the moment of dissolution), coincided with comparative maxima of the ethanol solution, it appears that the 4-methoxydiphenylamine sulfate formed was unstable. Apparently, this salt decomposed after standing for a long time in sulfuric acid, due to another chemical reaction that led to the oxidation of this diphenylamine derivative.

We consider that the oxidation of 4-methoxydiphenylamine occurs analogously to the oxidation of diphenylamine and 4-hydroxydiphenylamine. In this case, an azenium type of compound may be formed, and also, the condensation of the intermediate products may occur. We have investigated above the formation of an azenium type of salt by diphenylamine.

The end product of 4-methoxydiphenylamine oxidation and condensation may be given in the form of an azenium salt of dimethoxydiphenylbenzidine

or in the form of a dibasic sulfate.

The electrophoresis of the colored sulfuric acid solutions of diphenylamine, 4-hydroxydiphenylamine and 4-methoxydiphenylamine that we carried out with platinum electrodes at a voltage of 2-4 v, showed that the colored ions had positive charges.

The occurrence of a deep change in the substances when treated with concentrated sulfuric acid is confirmed by the fact that colored solutions of 4-hydroxydiphenylamine, 4-methoxydiphenylamine and diphenylamine, itself, did not lose their color when diluted many times with water, but only became weaker.

SUMMARY

1. It is possible to get some idea of the deep changes that occur in diphenylamine and its derivatives when treated with concentrated sulfuric acid and the kinetics of these processes from the changes in the absorption spectrum curves of sulfuric acid solutions of these substances relative to the time of standing.

2. In oxidizing diphenylamine, 4-hydroxy- and 4-methoxydiphenylamines, oxidation at the nitrogen first occurs with the formation of azenium salts, which give a characteristic band with an absorption maximum at 318-330 mμ for all the substances and with further oxidation and condensation colored products of the azenium salt of a benzidine derivative type are formed.

3. Electrophoresis confirmed the fact that the colored ions have positive charges.

4. The colored sulfuric acid solutions of all the substances kept their color even after being diluted with water many times. This indicates the stability of the colored ions.

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THE RELATION OF THE PROPERTIES OF LIGNIN CHLORO DERIVATIVES TO THE CHLORINATION CONDITIONS

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We have already showed in previous reports [1, 2] that the properties of chlorinated lignins are, to a considerable extent, determined not only by the amount of chlorine introduced into the lignin, but also by the conditions of chlorination: temperature, catalyst, medium, presence or absence of moisture during chlorination. We found that at a low temperature (12°) the aromatic nuclei of lignin molecules were chlorinated more rapidly than the side chains. Heating displaced the distribution of chlorine between the nuclei and side chains, accelerating chain chlorination. The catalyst (iron) hardly affected the chlorine distribution, though it is a dechlorinating agent.

The presence of moisture considerably affected the course of chlorination. To elucidate the effect of moisture in chlorination on the properties of lignin chloro derivatives, we compared chlorolignins prepared under various conditions with and without moisture. For the comparison we used samples prepared by the chlorination of dry lignin with a solution of chlorine in CCl_4 at 12 and 77°, chlorination of dry lignin in a current of chlorine and samples of chlorolignin prepared by chlorination of lignin in a water suspension at 12° and lignin containing 50% moisture at a temperature of 70-80° (as a result of an exothermal reaction).

EXPERIMENTAL

For the chlorination we used hydrolysis lignin from the Leningrad Hydrolysis Plant, which had been sieved and freed from tar by extraction with dichloroethane and from reducing substances and acids by washing with dilute soda solution and water [3]. The conditions for chlorinating lignin at 12° in a medium of CCl_4 and chlorine water were described previously [3].

Chlorination in CCl_4 with heating was accomplished by passing a current of chlorine through a rheometer at a rate of 4 liters per hour into a suspension of 15 g of lignin in 300 ml of boiling CCl_4 in a three-necked flask with a stirrer and a reflux condenser. Under these conditions the amount of chlorine introduced into the lignin was close to that calculated for a substitution reaction. The chlorine began to get through only after 22% of chlorine had been introduced into the lignin. However, even with a very large excess of chlorine (10 times the given amount) we were unable to introduce into the lignin more than 24.8% by this method.

Chlorination of wet lignin was accomplished by passing a stream of chlorine through the lignin in a glass reaction tube. 6 g of the lignin, containing 50% water (prepared by wetting air-dried lignin and keeping it for a day in a jar with a ground glass stopper), was placed in a glass tube 15 cm long and 2 cm diameter fitted with porous glass baffles, one sealed into a ground glass stopper, through which the gas was introduced and the other at the end of the tube. The end of the tube was connected through a ground glass joint to a gas outlet tube. The amount of chlorine introduced was determined with a rheometer. Chlorine was fed into the tube through a gas mixer at a rate of 4 liters per hour. During the chlorination, drops of water appeared on the walls of the vessel and the lignin became yellow soon after the beginning of the experiment. At the point of the reaction there was intensive heat evolution (70-80°). This effect extended 1-2 cm along the tube. Then this part gradually cooled and the reaction moved along further. The reaction gradually moved in this way along the whole tube over 37-40 minutes. After this free chlorine began to pass through and appeared in the water wash bottle, connected to the outlet tube. During the whole of the chlorination there was vigorous evolution of hydrogen chloride. At the end of the chlorination, the chlorolignin was washed with water. In this way we obtained 2 samples: 1st chlorinated over 45 minutes and the 2nd chlorinated with a large excess of chlorine for 2 hours.

TABLE 1

Chlorolignins Prepared by Dry Chlorination

Preparations of chlorolignin, conditions of chlorination (chlor.) and hydrolysis (hydr.)	Cl content (in %)	Cl loss (in %)	Molecular wt. of structural unit	Amount of functional groups in structural unit (in moles)					Yield (in %)	
				Cl	OH	CO	COOH	OCH_3	by weight	of theoretical
Starting lignin	—	—	180	—	0.97	0.49	0.05	0.61	—	—
Chlor. at 12° in CCl_4 1 hr	18.82	—	221.73	1.17	—	0.42	0.18	0.44	—	92.09
Hydr. H_2O	14.01	25.54	209.33	0.83	—	0.55	0.13	0.44	82.42	—
Hydr. 5% NaOH	10.40	44.74	200.89	0.59	1.18	0.54	0.26	0.46	78.50	—
Chlor. in boiling CCl_4 37 min.	18.28	—	220.26	1.13	0.92	0.30	0.22	—	125	93.96
Hydr. H_2O	12.32	32.6	205.03	0.71	0.95	0.35	0.12	—	88.96	—
Hydr. 5% NaOH	7.87	56.95	195.38	0.43	1.06	0.34	0.27	—	76.48	—
Chlor. in boiling $CCCl_4$ 3 hrs. with a large excess of chlorine	24.38	—	238.03	1.63	1.09	0.36	0.33	0.47	127.78	94.26
Hydr. H_2O	17.90	26.58	219.24	1.10	1.24	0.39	0.20	—	91.45	—
Hydr. 5% NaOH	9.63	60.50	199.18	0.54	1.09	0.31	0.35	—	67.34	—
Dry chlor. without sol. 2 hours	21.41	—	229.04	1.38	—	0.39	0.28	—	128.51	101.41
Hydr. H_2O	14.73	31.20	211.09	0.88	1.06	0.43	0.17	—	86.43	—
Hydr. 5% NaOH	10.21	52.31	200.47	0.58	1.17	0.37	0.38	—	74.24	—
Dry chlor. without solv. 4.5 hrs. with a large excess of chlorine	25.41	—	241.32	1.73	1.01	0.32	0.33	—	135.5	100.61
Hydr. H_2O	18.24	28.41	220.16	1.12	1.22	0.42	0.22	—	80.90	—
Hydr. 5% NaOH	10.00	60.64	200.00	0.56	1.12	0.52	0.38	—	70.20	—

TABLE 2

Chlorolignins Prepared in the Presence of H_2O

Preparation of chlorolignin, conditions of chlorination (chlor.) and hydrolysis (hydr.)	Cl content (in %)	Cl loss (in %)	Molecular wt. of structural unit	Amount of functional groups in structural unit (in moles)					Yield (in %)	
				Cl	OH	CO	COOH	OCH_3	by weight	of theoretical
Starting lignin		—	180.00	—	0.83	0.21	0.06	0.52	—	—
Chlor. in water suspension at 12°	24.02	—	236.90	1.62	—	0.51	0.54	0.1	—	95.81
Hydr. H_2O	19.46	18.98	223.49	1.22	0.76	0.58	0.48	0.1	—	—
Hydr. 5% NaOH	8.20	65.86	196.08	0.45	0.83	0.50	—	0.08	—	—
Starting lignin	—	—	180.00	—	0.97	0.49	0.05	0.61	—	—
Chlor. with 50% by a current of chlorine at 70-80° with an excess of chlorine for 45 min.	27.53	—	248.38	1.93	—	0.43	0.74	0.28	135.54	98.75
Hydr. H_2O	22.96	16.60	233.64	1.51	1.17	0.40	0.50	—	84.35	—
Hydr. 5% NaOH	9.25	66.40	198.35	0.52	1.14	0.47	0.46	—	52.03	—
Chlor. with 50% by a current of chlorine at 70-80° with an excess of chlorine for 2 hours	29.27	—	254.60	2.10	1.13	0.48	0.83	0.02	139.02	98.65
Hydr. H_2O	24.73	15.60	239.14	1.67	1.10	0.44	0.52	—	85.95	—
Hydr. NaOH	9.38	67.95	138.34	0.52	1.10	0.46	0.42	—	55.41	—

In the same apparatus we chlorinated dry lignin. Chlorine diluted with nitrogen (in one experiment 3 fold and in another 10 fold) was passed through lignin dried over P_2O_5 (6-12 g). The chlorine flow rate was 900 ml per hour. Chlorine got through during the whole of the reaction. The time of chlorination was 2 hours in the 1st experiment and 4.5 hours in the 2nd. At the end of the chlorination, excess chlorine and hydrogen chloride were flushed out with a current of nitrogen.

The data given in Tables 1 and 2 show that in the chlorination of dry lignin both in a CCl_4 suspension and in the tube, even with a large excess of chlorine, not more than 25% of chlorine could be introduced into the lignin. In chlorination of wet lignin at 70-80° with excess chlorine, we obtained samples, containing 27.53 and 29.27% chlorine. The chlorolignins obtained by chlorination of lignin in the presence of water contained only very small amounts of OCH_3 groups. The main part of the methoxyl groups was lost during the chlorination, while this did not occur in the chlorination of dry lignin. The presence of moisture in the chlorination had little effect on the content of OH groups. Moisture had a considerable effect on the COOH group content.

A sample, containing 1.62 moles of chlorine in the structural unit and prepared by chlorinating lignin with chlorine water at 12° using an amount of chlorine water calculated to introduce 2 moles of chlorine into the lignin, contained more than 0.5 mole of COOH per structural unit. Corresponding samples prepared by chlorination in the absence of moisture, contained half the amount of carboxyl groups (Tables 1 and 2). Chlorolignins, containing 1.93 and 2.10 moles of chlorine and prepared by chlorinating wet lignin, contained 0.74 and 0.83 mole of COOH per elementary unit respectively. Consequently, the presence of moisture in the chlorination considerably promotes the oxidation of lignin.

It is noticeable that chlorolignins, prepared under various conditions and containing various amounts of chlorine (more than 0.5 mole per structural unit) retain an amount of chlorine close to 0.5 mole after boiling with 5% NaOH solution. This indicates that during the chlorination of lignin the aromatic rings are chlorinated first of all and that in all cases the amount of firmly bound chlorine is approximately the same.

SUMMARY

1. Heating during chlorination displaced the distribution of chlorine between the lignin aromatic nuclei and side chains, accelerating chlorination of the chains.

2. The presence of moisture considerable affected the course of chlorination by increasing the oxidation reactions and this increased the number of carboxyl groups and decreased the number of methoxyl groups.

3. The hydrolysis of chlorolignins, prepared under any conditions and containing more than 0.5 mole of chlorine, with a 5% NaOH solution gave products containing about 0.5 mole of chlorine, which showed that the aromatic nuclei were chlorinated first and the amount of stably bound chlorine (in the nucleus) was approximately the same in all cases.

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THE CHLOROMETHYLATION OF 1-ALKYLNAPHTHALENES AND SOME TRANSFORMATIONS OF 4-CHLOROMETHYL-1-ALKYLNAPHTHALENES

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Among 1-alkylnaphthalenes only 1-methyl- and 1-isopropylnaphthalene have been chloromethylated so far [1]. In both cases the chloromethyl group went into position 4 in the naphthalene ring. In the present work 1-ethyl-, 1-n-propyl-, 1-isopropyl- and 1-n-butylnaphthalenes have been chloromethylated. The reactions were carried out using paraformaldehyde and hydrogen chloride in hydrochloric acid medium and in the presence of zinc chloride. The yield of chloromethyl-1-alkylnaphthalenes was 80-90%. By analogy it was to be expected that the compounds obtained were, as before, 4-chloromethyl-1-alkylnaphthalenes and this was confirmed in the course of further investigations. We were interested mainly in 1-alkylnaphthalene-4-carboxylic acids which have been investigated very little and which may, among other things, be utilized as starting materials in the synthesis of pharmacologically active compounds; the preparation of these acids from the easily accessible chloromethyl-alkylnaphthalenes appears to be simpler than by any other method. In addition, the structure of the alkylnaphthalene-carboxylic acids obtained in this way could be determined easily by comparison with other members of this series already known; this, in turn, would facilitate the elucidation of the structure of the original chloromethyl-alkylnaphthalenes. The direct transformation of chloromethylalkylnaphthalenes into the corresponding alkylnaphthalene-carboxylic acids by the oxidation of the chloromethyl group to a carboxyl group is difficult because the alkyl group also undergoes oxidation in the course of the reaction. This difficulty was circumvented as follows: the chloromethylated compounds were first treated with lead acetate, the acetoxymethyl-1-alkylnaphthalenes so obtained were saponified and the resulting hydroxymethyl-1-alkylnaphthalenes were submitted to oxidation. The yields of compounds obtained in the various stages are sufficiently high and the simultaneous oxidation of the alkyl group resulting in the formation of a dicarboxylic acid together with the monocarboxylic one was observed only during oxidation of 4-hydroxymethyl-1-ethylnaphthalene; however, the amount of dicarboxylic acid in this case was small (12%). We have also attempted to prepare hydroxymethyl-1-alkylnaphthalenes by the action of aqueous alkali on 4-chloromethyl-1-alkylnaphthalenes; however, the yield of hydroxymethyl-alkylnaphthalenes was small and decreased considerably with increasing size of the alkyl radical (for example, 4-hydroxymethyl-1-ethylnaphthalene was obtained in 20% yield; 4-hydroxymethyl-1-n-propylnaphthalene in 12% yield, and so on).

Oxidation of 4-hydroxymethyl-1-alkylnaphthalenes with permanganate in acetone solution proceeded without difficulty. By such treatment of all the above-mentioned chloromethyl-1-alkylnaphthalenes we have prepared the corresponding 1-alkylnaphthalene-monocarboxylic acids; the acid obtained from 4-hydroxymethyl-1-ethylnaphthalene was found to be identical with 1-ethylnaphthalene-4-carboxylic acid described in the literature [2], while 1-butylnaphthalene-4-carboxylic acid obtained from 4-hydroxymethyl-1-butylnaphthalene was identical with the acid prepared by us earlier from 4-iodo-1-n-butylnaphthalene [3].

The structure of the chloromethyl derivative of 1-isopropylnaphthalene was confirmed by comparison with 4-chloromethyl-1-isopropylnaphthalene described in the literature. Confirmation of the structure of 4-chloromethyl-1-n-propylnaphthalene was not attempted as there were no reasons to suppose that chloromethylation of this hydrocarbon under these conditions could proceed in any other direction.

4-Chloromethyl-1-alkylnaphthalenes were used by us for the synthesis of (1-alkylnaphthyl-4)-methyl-N-di-(chloroethyl)-amines

$$[R—C_{10}H_6—CH_2N(CH_2CH_2Cl)_2],$$

which are of interest in cancer treatment. These compounds were obtained by interacting 4-chloromethyl-1-alkylnaphthalenes with diethanolamine followed by substitution of the hydroxyl groups of (1-alkylnaphthyl-4)-methyl-N-di-(hydroxyethyl)-amines by chlorine, using thionyl chloride. In reactions of 4-chloromethyl-1-alkylnaphthalene with diethanolamine we also observed decreasing mobility of the chlorine atom with increasing size of the alkyl radical. It was impossible to obtain (1-alkylnaphthyl-4)-methyl-N-di-(hydroxyethyl)-amines in the pure state as these compounds are unstable either as the free bases or in the form of their salts (hydrochlorides and picrates) and rapidly change to viscous masses; for this reason the preparation of (1-alkylnaphthyl-4)-methyl-N-di-(chloroethyl)-amines was conducted without the isolation of the intermediate compounds.

EXPERIMENTAL

The preparation and properties of derivatives of 1-n-butylnaphthalene mentioned in the general part have been described in detail in the experimental part. The data relating to the preparation and properties of similar derivatives of other 1-alkyl-naphthalenes are given in the table as the corresponding reactions, isolation and purification of the compounds were carried out in a manner analogous to that followed in the preparation of similar derivatives of 1-n-butylnaphthalene.

4-Chloromethyl-1-n-butylnaphthalene. A mixture of 25 g of 1-butylnaphthalene, 17 g of paraformaldehyde, 6 g of zinc chloride and 60 ml of concentrated hydrochloric acid was heated during 6 hours at 65-70°, a slow current of hydrogen chloride being passed into the reaction mixture. The mixture was then poured into water and the oily substance which separated was extracted with benzene. The benzene solution was washed with water, sodium carbonate solution and again with water and was dried over potassium hydroxide. The solvent was removed and the residue distilled in vacuo. The first fraction, 3 g, was collected between 100 and 134° (1 mm), the second fraction, 24.8 g, between 135 and 141° (1 mm).

The first fraction was redistilled and there was obtained 0.5 g of 1-butyl-naphthalene boiling at 99-100° (1 mm) (picrate, m. p. 64-65°) and 2.1 g of a substance boiling at 130-140° (1 mm). The latter was combined with the second fraction and the mixture was distilled. There was obtained 0.7 g of a substance boiling at 110-120° (1 mm) (a mixture of 1-butylnaphthalene and 4-chloromethyl-1-butylnaphthalene) and 25.6 g (81%) of 4-chloromethyl-1-butylnaphthalene boiling at 139-140° (1 mm). The latter was redistilled for analysis. Colorless liquid, b. p. 140-141° (1 mm); darkens on exposure to air, irritant to skin, soluble in most organic solvents, insoluble in water.

Found %: C 77.17; H 7.11; Cl 15.27. $C_{15}H_{17}Cl$. Calculated %: C 77.40; H 7.36; Cl 15.23.

This method was used in preparing all the other 4-chloromethyl-1-alkylnaphthalenes (yields 80-90%). Their properties are similar to those of 4-chloromethyl-1-butylnaphthalene (Table 1).

TABLE 1

4-Chloromethyl-1-alkylnaphthalenes $R-C_{10}H_6-CH_2Cl$

R	Weights of reagents taken (g)				Heating period (hours)	Melting point	Found (%)			Calcd. (%)		
	1-alkyl-naphthalene	Paraformaldehyde	Zinc chloride	Hydrochloric acid (ml)			C	H	Cl	C	H	Cl
C_2H_5 . . .	25	16	5	50	8	119—120° * (0.5 mm)	76.15	6.52	17.06	76.27	6.40	17.32
n-C_3H_7 . .	20	15	5	50	6	140—141 (1 mm)	77.08	7.12	16.28	76.87	6.91	16.21
iso-C_3H_7	15	15	4.5	50	6	126—127 (0.5 mm)	77.01	6.81	—	76.87	6.91	16.21

* The substance crystallized on standing and was recrystallized from alcohol, m. p. 84-85°.

TABLE 2

4-Acetoxymethyl-1-alkylnaphthalenes $R-C_{10}H_6CH_2OCOCH_3$

R	Weights of reagents taken (g)			Heating period at 90° (hours)	Melting point	Found (%)		Calcd. (%)	
	4-chloromethyl-1-alkylnaphthalene	Lead acetate	Acetic acid (ml)			C	H	C	H
C_2H_5	2	1.8	30	2	134—135° (0.5 mm)	78.97	6.92	78.92	7.06
n-C_3H_7	2	2	120	2	150—151 (1 mm)	79.40	7.4	79.31	7.98
iso-C_3H_7	2	2	120	2	149—150 (0.5 mm)	79.30	7.2	79.31	7.98

4-Acetoxymethyl-1-n-butylnaphthalene. A solution of 2 g of 4-chloromethyl-1-n-butylnaphthalene and 2 g of lead acetate in 40 ml of glacial acetic acid was heated for two hours at 90°. The reaction mixture was then diluted with water and the oily substance which separated was extracted with ether. The ether solution was washed with water, sodium carbonate solution and again with water and dried over sodium sulfate. The ether was removed and the residual substance was distilled twice in vacuo. There was obtained 1.85 g (84.1%) of 4-acetoxymethyl-1-butylnaphthalene boiling at 149-150° (1 mm). The substance was redistilled before analysis. Colorless liquid, b. p. 149.5-150° (1 mm), odorless, darkened on exposure to air, soluble in most organic solvents, insoluble in water.

Found %: C 79.76; H 7.71. $C_{17}H_{20}O_2$. Calculated %: C 79.70; H 7.80.

All the other 4-acetoxymethyl-1-alkylnaphthalenes were prepared by the above method (yields 80-90%). Their properties are similar to those of 4-acetoxymethyl-1-butylnaphthalene (Table 2).

TABLE 3

4-Hydroxymethyl-1-alkylnaphthalenes $R-C_{10}H_6-CH_2OH$

R	Weights of reagents taken (g)			Period of refluxing (hours)	Melting point	Found (%)		Calcd. (%	
	4-acetoxymethyl-1-alkylnaphthalene	Alkali	Alcohol (ml)			C	H	C	H
C_2H_5	5	1.6 (KOH)	30	2	81.5—82°	84.14	7.62	83.83	7.57
n-C_3H_7 . . .	5	1.8 (NaOH)	30	2	88.5—89	83.94	7.95	83.95	8.05
iso-C_3H_7 . . .	4	1.4 (KOH)	25	2	64—65	83.66	8.20	83.95	8.05

* For analysis the compounds were recrystallized several times from petroleum ether or from petrol.

4-Hydroxymethyl-1-n-butylnaphthalene. A solution of 6 g of 4-acetoxymethyl-1-n-butylnaphthalene and 1.8 g of potassium hydroxide in 40 ml of ethyl alcohol was refluxed for 30 minutes. The mixture was diluted with water and the crystals which separated were filtered off and washed with water. After recrystallization from petroleum ether there was obtained 1.8 g of a substance melting at 88-89°. Evaporation of the solvent gave a further 0.1 g of a substance melting at 87-88°; total yield, 4.9 g (98%). For analysis the 4-hydroxymethyl-1-butylnaphthalene obtained was recrystallized from petroleum ether. Colorless needles, m. p. 89.5-90°, soluble in alcohol, acetone, chloroform and other organic solvents, insoluble in water.

Found %: C 83.75; H 8.26. $C_{15}H_{18}O$. Calculated %: C 84.07; H 8.46.

The other 4-hydroxymethyl-1-alkylnaphthalenes were prepared by the same method (yields, 90-95%) (Table 3).

1-n-Butylnaphthalene-4-carboxylic acid. To a solution of 1 g of 4-hydroxymethyl-1-butylnaphthalene in 40 ml of acetone there was added 1.1 g of potassium permanganate and the mixture was heated for two hours at the boiling point of acetone. The brown solid which separated was filtered off and washed with acetone. It was then refluxed repeatedly with water and filtered. The aqueous filtrates were combined, concentrated to a small volume and acidified with hydrochloric acid until acid to Congo red. The crystalline solid which separated was filtered off, washed with water and dried. After recrystallization from aqueous alcohol there was obtained 0.8 g of a substance melting at 145-146°. After evaporating the alcoholic mother liquor there was obtained another 0.13 g of the substance, m. p. 144-145°, giving a total yield of 0.93 g (89.6%). After two recrystallizations from aqueous alcohol 1-butylnaphthalene-4-carboxylic acid was obtained as colorless needles, m. p. 148-148.5°, soluble in benzene, toluene, alcohol and other organic solvents, insoluble in petrol or water. Mixture of the substance with the acid obtained previously from 4-iodo-1-butylnaphthalene melted at 148-148.5°.

Found %: C 78.82; H 7.31. $C_{15}H_{16}O_2$. Calculated %: C 78.91; H 7.07.

The other 4-alkylnaphthalene-4-carboxylic acids were prepared by the same method (yields, 90-95%). Their properties are similar to those of 1-n-butylnaphthalene-4-carboxylic acid (Table 4).

TABLE 4

Alkylnaphthalene-4-carboxylic Acids $R-C_{10}H_6-COOH$

R	Weights of reagents taken (g)			Melting point	Found (%)		Calcd. (%)	
	4-hydroxymethyl-1-alkylnaphthalene	Potassium permanganate	Acetone (ml)		C	H	C	H
C_2H_5	1	1.4	40	129—130°	—	—	—	—
n-C_3H_7	1	0.78	30	141—142	78.54	6.59	78.49	6.58
iso-C_3H_7	5	4.8	60	153—153.5	78.64	6.69	78.49	6.58

* The compounds were recrystallized from aqueous alcohol.

TABLE 5

Hydrochlorides of (1-Alkylnaphthyl-4)-methyl-N-di-(chloroethyl)-amines
$R-C_{10}H_6-CH_2N(CH_2CH_2Cl)_2HCl$

R	Weights of reagents taken (g)				Melting point	Found (%)				Calcd. (%)			
	4-chloromethyl-1-alkylnaphthalene	Diethanolamine	Anhydrous benzene (ml)	Thionyl chloride		C	H	N	Cl	C	H	N	Cl
C_2H_5 . . .	5	7.3	15	30	147—148°	59.08	6.22	3.88	10.13	58.89	6.39	4.03	10.33
n-C_3H_7 . .	13.2	6.8	15	26	158.5—159	60.33	6.68	4.27	9.88	59.23	6.70	3.88	9.89
iso-C_3H_7 .	13	6.9	15	30	129.5—130.5	60.7	6.96	3.80	9.86	59.23	6.70	3.88	9.89

* For analysis the compounds were recrystallized twice from anhydrous alcohol.

(1-n-Butylnaphthyl-4)-methyl-N-di-(chloroethyl)-amine hydrochloride. To 6.2 g of diethanolamine was added 15 g of 4-chloromethyl-1-n-butylnaphthalene and the mixture was heated for 6.5 hours at 90°. It was then cooled to room temperature and there was added 15 ml of anhydrous benzene and, slowly and dropwise, 30 g of thionyl chloride. The mixture was then heated at 68-70° for 1.5 hours, the benzene and thionyl chloride were removed and the residue was treated with potassium carbonate solution. The oily substance which separated was extracted with ether, the ether extract was washed with water and dried over potassium carbonate. To the ether solution was added a solution of hydrogen chloride, also in ether. The crystals which separated were filtered off and washed with ether. After recrystallization from anhydrous alcohol there was obtained 16.6 g of the hydrochloride of (1-n-butylnaphthyl-4)-methyl-N-di-(chloroethyl)-amine, m. p. 125-129°. On evaporation of the alcoholic mother liquor there separated another 1.6 g of the substance, m. p. 127-128°; total yield 18.2 g (78.1%). For analysis the substance was recrystallized twice from anhydrous alcohol. Colorless crystals, m. p. 129.5-130.5°, soluble in alcohol, glacial acetic acid, insoluble in benzene, ether, and water.

Found %: C 60.70; H 6.96; N 3.80; Cl 28.49. $C_{19}H_{25}NCl_2 \cdot HCl$. Calculated %: C 60.89; H 6.99; N 3.73; Cl 28.38.

The free base was isolated as a viscous oil, soluble in most organic solvents and insoluble in water. Decomposition took place when the substance was distilled in vacuo.

The hydrochlorides of the other amine analogs were prepared by the above method in yields of 78-85%. The properties of the hydrochlorides and of the free bases are similar to the hydrochloride of (1-n-butylnaphthyl-4)-methyl-N-di-(chloroethyl)-amine and the free base obtained therefrom (Table 5).

SUMMARY

The authors have described the preparation of 4-chloromethyl-1-alkylnaphthalenes, 1-alkylnaphthalene-4-carboxylic acids and (1-alkylnaphthyl-4)-methyl-N-di-(chloroethyl)-amines with the following alkyl radicals: C_2H_5, n-C_3H_7, iso-C_3H_7 and n-C_4H_9.

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INVESTIGATIONS IN THE FIELD OF DYES FOR ACETATE SILK AND SYNTHETIC FIBERS

I. 1,5- AND 1,8-ACYLAMINO-HYDROXYANTHRAQUINONES

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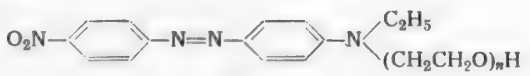
Acetylcellulose differs markedly from natural fibers in its behavior towards dyes. Most direct and acid dyes which are widely used in dyeing cotton, viscose and wool, do not dye acetate silk. This is due to the characteristic structure of acetylcellulose in which most of the hydroxy-groups are blocked by acetyl radicals. In contemporary theories the dyeing of acetate silk is regarded as an extraction of the dye by the solid solvent (acetate silk) from the dye vat. Comparing acetylcellulose with other esters of acetic acid Mayer points out that substances which are removed from their aqueous solutions by ethyl acetate are also absorbed by artificial silk fibers [1]. On the basis of this one would therefore expect that the solubility of a given colored compound in ethyl acetate could be used as a preliminary indication of its ability to dye acetate silk. However, acetate silk fibers do not only represent a solid solvent; as a result of the extension of the fibers which takes place during spinning, the molecules of acetylcellulose assume an elongated shape and are oriented in the direction of the length of the fiber and contain repeating units of about 10.3 A [2]. A straight comparison of ethyl acetate and acetylcellulose fibers as a liquid and a solid solvent, respectively, does not account for this phenomenon and must therefore be regarded as only a first approximation.

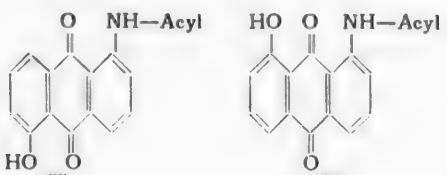
On the other hand, Green and Ellis, in the course of investigations of dyes which could be used to dye acetate silk, have established that the presence in the molecule of the dye of a hydroxy or amino group, low molecular weight and an almost neutral or basic character facilitate the dyeing process; vice versa, a relatively high molecular weight, acidic nature (in particular the presence of sulfo groups) and good solubility in water have the opposite effect [3]. Contrary to these findings Wahl has, in the course of investigations of properties of azo-dyes of the general formula (I) (n = from 0 to 3)



(I)

found that the rate of extraction is greatest in the case of dyes with n = 2 or 3 while the maximum intensity of coloration was obtained with the compound where n = 2, the amount absorbed in this case being 56 mg per g of acetate silk fiber [4].

In recent years a number of patents [5,6] have described 1,5- and 1,8-acylamino-hydroxyanthraquinones of the general formulas (II) and (III) as yellow dyes for acetate silk.



(II) (III)

The higher homologs of these compounds (containing a longer acyl chain) are also suitable as dyes for fats and oils [6]. It has been observed that mixtures of two such dyes are more effective than the individual compounds separately [7]. These dyes represent, therefore, suitable compounds for the investigation of their dyeing properties and in particular for the investigation of the extractability of the dye by acetate silk fiber as a function of the length of the acyl radical (and hence, of molecular weight and size) since variation of the acyl radical has hardly any effect on molecular absorption spectra of the dyes in the range of 350-500 mμ.

TABLE 1

1,5- and 1,8-Acylamino-hydroxyanthraquniones

Acyl radical	Yield (in %)	Melting point	Empirical formula	N (%)	
				Found	Calcd.
1-Acylamino-5-hydroxyanthraquinones (II)					
acetyl	95.5	228.2—228.6°	$C_{16}H_{11}O_4N$	5.09, 4.84	4.98
propionyl	58.3	195.8—196.2	$C_{17}H_{13}O_4N$	4.49, 4.61	4.74
butyryl	78.0	172.4—173.1	$C_{18}H_{15}O_4N$	4.10, 4.35	4.53
valeryl	79.6	143.5—145.0	$C_{19}H_{17}O_4N$	4.16, 4.14	4.33
isovaleryl	53.4	147.0—147.5	$C_{19}H_{17}O_4N$	3.92, 4.12	4.33
caproyl	89.8	140.5—141.5	$C_{20}H_{19}O_4N$	4.11, 4.07	4.15
capryl	—	136.5—137.5	$C_{22}H_{23}O_4N$	3.55, 3.78	3.83
1-Acylamino-8-hydroxyanthraquinones (III)					
acetyl	92.1	216.8—218.0	$C_{16}H_{11}O_4N$	5.06, 5.06	4.98
propionyl	67.4	177.2—179.2	$C_{17}H_{13}O_4N$	4.51, 4.53	4.74
butyryl	76.4	162.0—163.4	$C_{18}H_{15}O_4N$	4.30, 4.32	4.53
valeryl	81.8	120.0—121.5	$C_{19}H_{17}O_4N$	4.39, 4.28	4.33
isovaleryl	82.0	136.5—137.5	$C_{19}H_{17}O_4N$	3.95, 4.00	4.33
caproyl	84.5	118.0—119.6	$C_{20}H_{19}O_4N$	3.94, 4.14	4.15
capryl	82.0	105.0—108.0	$C_{22}H_{23}O_4N$	3.68, 3.65	3.83

1,5- and 1,8-amino-hydroxyanthraquinones — the starting materials for the synthesis of these dyes — may be prepared by several methods, namely: a) heating the product of condensation of diazotized 1,5- or 1,8-diaminoanthraquinone and ammonia with concentrated sulfuric acid [8]; b) heating, for five hours in a sealed tube, at 145°, a paste of 1,8-dihydroxyanthraquinone which has been saturated with ammonia at 0° [9]; c) nitrating the potassium salt of 1-anthraquinone-sulfonic acid, [11, 12] separating the resulting mixture of 1,5- and 1,8-nitroanthraquinone-sulfonic acids, reducing the latter acids with sodium sulfite to the corresponding amino-sulfonic acids [11] and heating the 1,5- or 1,8-aminoanthraquninone-sulfonic acids obtained in aqueous solution with milk of lime or barium hydroxide at 160-170° under pressure [10].

The first two methods did not give satisfactory results as the reactions proceeded with difficulty and were accompanied by considerable tarring; on the other hand the last method was found to be very suitable and the purity of the aminohydroxyanthraquinones obtained was as a rule determined by the quality of the starting amino-anthraquinone-sulfonic acids.

1,5- and 1,8-acylamino-hydroxyanthraquinones were obtained by the interaction of 1,5- and 1,8-amino-hydroxyanthraquinones with acyl chlorides of the corresponding carboxylic acids in pyridine (Table 1). The absorption spectra of these dyes in ethyl acetate were recorded on an SF-4 spectrophotometer. All the spectra exhibit an absorption maximum at 410 mμ and the molecular extinctions are very close to each other: in the case of the 1,5-derivatives log ε varies from 3.66 to 3.73 and in the case of 1,8-derivatives from 3.63-3.69.

It was to be expected that absorption spectra of acyl derivatives of either 1,5- or 1,8-amino-hydroxyanthraquinone would be very similar since a change of the acyl radical would have little effect on the electron distribution in the molecule. More unexpected was the discovery that absorption spectra of the dyes of both series of derivatives were almost identical. This may be explained by the fact that the individual benzene rings in the

anthraquinone structure have little effect on each other. To exemplify this the absorptions of 1,5- and 1,8-acetylamino-hydroxyanthraquinones are shown in Table 2.

TABLE 2

Molecular Extinction Coefficients (log ϵ) of Isomeric Acetylamino-hydroxyanthraquinones

λ (in mμ) / Compound	log ε									
	360	380	390	400	410	420	430	440	460	480
1,5-Acetylamino-hydroxy-anthraquinone	3.42	3.58	3.65	3.69	3.70	3.68	3.61	3.51	3.07	2.23
1,8-Acetylamino-hydroxy-anthraquinone	3.42	3.59	3.65	3.68	3.69	3.67	3.61	3.52	3.06	2.35

TABLE 3

Molecular Extinction Coefficients (for λ_{max} 410 mμ), Solubility in Ethyl Acetate at 25° and Dyeing Power of Acylamino-hydroxyanthraquinones

Acyl radical	Molecular extinction, log ε	Solubility in ethyl acetate (g/100 g solvent)	Dyeing power
1-Acylamino-5-hydroxyanthraquinones (II)			
acetyl	3.70	0.225	(+)
propionyl	3.67	0.934	(+)
butyryl	3.68	1.480	(+)
valeryl	3.73	3.250	(+)
isovaleryl	3.66	5.830	(+)
caproyl	3.66	2.717	(−)
capryl	3.66	2.261	(−)
1-Acylamino-8-hydroxyanthraquinones (III)			
acetyl	3.69	0.122	(+)
propionyl	3.66	0.784	(+)
butyryl	3.65	0.887	(+)
valeryl	3.66	1.118	(+)
isovaleryl	3.65	1.539	(+)
caproyl	3.64	0.768	(−)
capryl	3.63	0.354	(−)

Note: (+++) − strong color, (++) − good color, (+) − weak, (−) − very faint, (−) − no color.

In order to investigate the relationship between dyeing characteristics and solubility of the dyes we have dyed acetate silk with these dyes and we have determined their solubility in ethyl acetate at 25°. It was found that only the derivatives of acetic, propionic and butyric acids exhibited good dyeing properties; derivatives of valeric and isovaleric acids were weak dyes, while the derivatives of caproic and caprylic acids hardly dyed acetate silk at all. These variations in dyeing power bear no direct relationship to the solubility of the dyes in ethyl acetate which reaches a maximum in the case of derivatives of isovaleric and valeric acids and is between three and ten times greater even in the case of the capryl derivatives, which do not dye the silk, than the solubility of the corresponding acetyl derivatives (Table 3).

EXPERIMENTAL

1-Amino-8-hydroxyanthraquinone. 37 g of 1-aminoanthraquinone-sulfonic-(8) acid (in the form of a 40% paste of its potassium or sodium salt), 85 g of crystalline barium hydroxide and 205 ml of water was heated in an autoclave for six hours at 160° under a pressure of about 6 atmos. The precipitate of the barium salt of 1-amino-8-hydroxyanthraquinone (reddish purple crystals) was filtered off, the paste was mixed with 400 ml of water and acidified, while boiling, with 700 ml of pure dilute (1 : 2) hydrochloric acid. The precipitate was filtered and washed free of barium salts with water. After crystallization from alcohol 14.1 g (57%) of 1-amino-8-hydroxyanthraquinone was obtained as dark purple needles, m. p. 230-231.4°; literature [10], m. p. 230°.

Found %: N 5.69, 5.64. $C_{14}H_9O_3N$. Calculated %: N 5.85.

The substance dissolves in toluene with yellow coloration, in aqueous ammonia with wine coloration and in caustic alkalis with purple coloration. The (violet) barium salt is insoluble in water, difficultly soluble in boiling hydrochloric acid giving rise to yellow coloration. In concentrated sulfuric acid it gives rise to yellow coloration which on addition of a drop of formalin turns violet. On diazotization and boiling of the solution of the diazonium salt the latter is transformed into 1,8-dihydroxyanthraquinone, m. p. 192-193° (subl.); literature [13], m. p. 193°.

1-Amino-5-hydroxyanthraquinone was obtained in a similar manner by heating 1-aminoanthraquinone-sulfonic acid-(5) with the other reagents during six hours at 165°. After crystallization from alcohol the compound was obtained, in 80% yield, as reddish brown needles, m. p. 211.0 to 213.4°; literature [10], 210°. It dissolves in alcohol with reddish-brown coloration, as well as in aqueous ammonia, caustic alkalis and alkaline carbonates, as does the 1,8-isomer. In concentrated sulfuric acid it gives rise to an orange coloration which turns blue on addition of a drop of formalin. On diazotization and boiling of the diazonium salt solution it is transformed into 1,5-dihydroxyanthraquinone, m. p. 278.4-280.2° (subl.); literature [14], m. p. 280°.

1-Acetylamino-8-hydroxyanthraquinone. To a suspension of 2.1 g of 1-amino-8-hydroxyanthraquinone in 20.5 ml of anhydrous pyridine was added dropwise 2.5 g of acetyl chloride over 10 minutes. During the addition the temperature rose to 54-60°. The reaction mass was stirred for 1 hour at 60° and its color gradually changed from deep red to yellow. It was then diluted with 20 ml of methanol, cooled, filtered and the residue washed with methanol. There was obtained 3.37 g of 1-acetylamino-8-hydroxyanthraquinone in the form of yellow needles, m. p. 228.2-228.6° (from a mixture of alcohol and acetic acid).

Acetylation of 1-amino-5-hydroxyanthraquinone and the subsequent acylation with chlorides of other fatty acids was carried out in analogous manner. The melting points and analyses of the compounds obtained are given in Table 1.

SUMMARY

1. The absorption spectra solubility in ethyl acetate and dyeing power of 1-acylamino-5- and -8-hydroxyanthraquinones which are used as dyes for acetate silk, have been investigated.

2. It was found that the dyeing power of these dyes towards acetate silk decreases sharply with increasing length of the acyl radical.

3. Contrary to established views, this decrease in dyeing power is in no way related to the solubility of these dyes in ethyl acetate.

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THE REACTION OF AMINES WITH PENTABORANE

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The reactions of amines with diborane are described in the literature [1-3]. Interaction between amines and diborane takes place in two ways: at low temperatures the diborane splits into borine groups to which the amine becomes attached forming complex compounds of the type BH_3NR_3 – the borazanes; when heated above 100° these compounds eliminate 1 or 2 molecules of hydrogen with the formation of borazenes $(BH_2NR_2)_2$ or borazines $(BHNR)_3$. The reactions of amines with pentaborane have been little studied. The literature describes only the reaction of stable pentaborane with trimethylamine, which is accompanied by the formation of the complex $B_5H_9 \cdot 2N(CH_3)_3$ [4]. This last compound when heated gives trimethylaminoborine and other compounds which have not been characterized. No other data on the reactions of amines with pentaborane have been published.

In a study of the reactions of diethyl- and triethylamine, dimethyl- and trimethylamine with pentaborane, we have established that as a result of a primary reaction at low temperatures (up to 0°), direct additions of the amine to the pentaborane takes place with the formation of complex compounds of the type $B_5H_9 \cdot nNHR_2$ for the secondary amines, where n = 2, 3, 4, 5, and $B_5H_9 \cdot 2NR_3$ for the tertiary amines.

In the complexes of secondary and tertiary amines obtained, the minimum value of n = 2, no matter how much excess pentaborane is taken, which is evidently connected with the nature of the complex-forming bond and the structure of pentaborane. For the tertiary amines the value n = 2 is also the maximum value, no matter how much excesss amine is taken, while for the secondary amines the maximum value is n = 5.

The reactions are accompanied by a considerable evolution of heat in the case of the secondary amines and by a smaller evolution of heat in the case of the tertiary amines. The complexes of pentaborane with the secondary amines under normal conditions are transparent liquids, while the complexes with the tertiary amines are solid white substances. The formation of the complexes is accompanied by a considerable contraction of the initial volumes of the starting components, as can be seen from the data in Table 2.

The complex compounds of pentaborane with alkylamines are stable at low temperatures up to 0°. When the temperature is raised, decomposition of the complexes takes place with evolution of hydrogen, breakdown of the pentaborane molecule and the formation of alkylamino derivatives of diborane and borine. This process goes fully to completion when the complexes are heated at 100-120° for 1.5-2 hours. The composition of the products obtained depends on the composition of the original complex and is given in the experimental part. On the basis of the composition and relative proportions of the alkylamino boron derivatives obtained it is possible to put forward the following equations for the main reactions of thermal decomposition of the complexes of pentaborane and alkylamines.

$$5B_5H_9 \cdot 2NHR_2 \rightarrow 7B_2H_5NR_2 + 2BH_2NR_2 + 2H_2 + \text{polymer} \quad (1)$$

$$B_5H_9 \cdot 3NHR_2 \rightarrow 2B_2H_5NR_2 + BH_2NR_2 \quad (2)$$

$$B_5H_9 \cdot 4NHR_2 \rightarrow B_2H_5NR_2 + 3BH_2NR_2 + H_2 \quad (3)$$

$$B_5H_9 \cdot 5NHR_2 \rightarrow 5BH_2NR_2 + 2H_2 \quad (4)$$

$$2B_5H_9 \cdot 2NR_3 \rightarrow 3BH_3NR_3 + \text{polymer} \quad (5)$$

As the number of moles of amine in the original complex is increased, the borine derivative content in the products of the decomposition of the complex increases while the diborane derivative content decreases. Diethylaminodiborane $B_2H_5N(C_2H_5)_2$ and triethylaminoborine $BH_3N(C_2H_5)_3$, obtained in the reaction products, are described for the first time; the physico-chemical properties of these compounds are given in the experimental part.

It has been established that diethylaminodiborane reacts with amines according to the equation

$$B_2H_5N(C_2H_5)_2 + NH(C_2H_5)_2 \xrightarrow{-20^\circ} B_2H_5N(C_2H_5)_2 \cdot NH(C_2H_5)_2 \rightarrow$$
$$\xrightarrow{120^\circ} 2BH_2N(C_2H_5)_2 + H_2$$

and is quantitatively hydrolyzed by water acidified with hydrochloric acid

$$B_2H_5N(C_2H_5)_2 + 6H_2O + HCl \rightarrow 2B(OH)_3 + NH(C_2H_5)_2 \cdot HCl + 5H_2$$

The latter reaction was used for the quantitative analysis of diethyl- and dimethylaminodiborane.

EXPERIMENTAL

I. The preparation of the pentaborane–alkylamine complexes.

All the experiments were carried out using pentaborane which had been carefully purified by distillation on a fractionating column. The distilled pentaborane had the following constants [5]: b.p. 60.0-60.2° at 760 mm, m.p. −46.5°, d_4^{20} 0.626.

Found %: B 85.6; H 14.3. B_5H_9. Calculated %: B 85.64; H 14.56.

The liquid amines $NH(C_2H_5)_2$ and $N(C_2H_5)_3$ were given a preliminary treatment with ignited calcium oxide and distilled. The gaseous amines $NH(CH_3)_2$ and $N(CH_3)_3$ were passed through a system of drying columns containing calcium oxide.

The reactions were carried out in an atmosphere of nitrogen out of contact with air or moisture.

a) The preparation of the diethylamine–pentaborane complexes. The preparation of $B_5H_9 \cdot 2NH(C_2H_5)_2$. 9.5 g (0.15 mole) pentaborane was introduced into the reaction vessel (Figure 1), cooled initially to −15°, and 11 g (0.15 mole) of diethylamine added gradually from a dropping funnel with shaking. The temperature in the reaction mixture was controlled by regulating the rate of addition of diethylamine and was maintained between −3 and −5°.

Each portion added reacted immediately, as determined by the increase in temperature. This phenomenon was observed throughout the whole process of addition of the amine. The reaction took place with no evolution of hydrogen and no formation of precipitate. The excess pentaborane was vacuum distilled at 1-2 mm from the reaction liquid obtained, the temperature in the bath raised gradually from −15 to +5° and the liquid maintained at this temperature for 3 hours and at room temperature for a further hour. The distillate, collected in a receiver at a temperature of −196°, amounted to 5 g (0.079 mole) and proved to be pure pentaborane. 4.5 g (0.071 mole) of pentaborane had thus reacted, which corresponds to a ratio $B_5H_9 : NH(C_2H_5)_2 = 1 : 2$.

The other complexes of diethylamine and pentaborane were prepared in similar fashion. For the preparation of $B_5H_9 \cdot 3NH(C_2H_5)_2$ and $B_5H_9 \cdot 4NH(C_2H_5)_2$ the starting materials were taken in stoichiometric proportions. For the preparation of $B_5H_9 \cdot 5NH(C_2H_5)_2$ an excess of 7 moles of diethylamine to 1 mole of pentaborane was taken; the amine which did not react was distilled off in vacuo. In the same way it was established that B_5H_9 adds on no more than 5 molecules of amine. The data on the complexes obtained are given in Table 1.

b) The preparation of triethylamine–pentaborane complexes. The experiment was carried out in the apparatus shown in Figure 1. The ratio of the components taken for the reaction was $B_5H_9 : N(C_2H_5)_3 = 1 : 5.6$ g pentaborane was added with cooling to 48 g triethylamine. The reaction proceeded smoothly with no evolution of hydrogen. The temperature in the reaction mass was raised slowly and reached −5° at the end of the reaction.

TABLE 1

Pentaborane–Amine Complexes

Composition of complex	Yield (%)	Analysis (%)							
		Found				Calculated			
		B	N	C	H	B	N	C	H
$B_5H_9 \cdot 2NH(C_2H_5)_2$	98	24.93	13.14	48.34	14.32	25.14	13.37	48.87	14.5
$B_5H_9 \cdot 3NH(C_2H_5)_2$	99	19.05	15.1	50.7	15.0	19.16	14.87	50.98	14.98
$B_5H_9 \cdot 4NH(C_2H_5)_2$	97	15.0	15.9	53.8	15.2	15.19	15.75	54.01	15.02
$B_5H_9 \cdot 5NH(C_2H_5)_2$	99	12.75	16.26	56.0	15.1	12.60	16.40	56.4	15.0
$B_5H_9 \cdot 2N(C_2H_5)_3$	99	19.62	10.6	54.75	14.91	20.24	10.55	54.24	14.8
$B_5H_9 \cdot 2NH(CH_3)_2$	97	35.0	18.15	31.9	15.0	35.3	18.2	31.3	15.1
$B_5H_9 \cdot 3NH(CH_3)_2$	98	27.5	21.4	37.0	14.8	27.28	21.2	36.32	15.2
$B_5H_9 \cdot 4NH(CH_3)_2$	97	21.9	23.1	40.0	15.05	22.2	23.01	39.5	15.3
$B_5H_9 \cdot 5NH(CH_3)_2$	99	18.7	24.3	41.25	15.5	18.76	24.29	41.6	15.37
$B_5H_9 \cdot 2N(CH_3)_3$	97	29.5	15.35	40.2	15.1	29.83	15.44	39.71	15.0

TABLE 2

Composition of complex	d_4^0	Volume (ml/mole B_5H_9)		Contraction (ml/mole B_5H_9)	Viscosity (centistokes)
		of starting materials	of complex obtained		
$B_5H_9 \cdot 2NH(CH_3)_2$	0.777	231.4	197.5	33.9	22.7
$B_5H_9 \cdot 3NH(CH_3)_2$	0.792	297.7	250.7	47.7	38.1
$B_5H_9 \cdot 4NH(CH_3)_2$	0.787	364.2	309.0	55.2	30.0
$B_5H_9 \cdot 5NH(CH_3)_2$	0.773	430.2	373.0	57.2	14.0
$B_5H_9 \cdot 2NH(C_2H_5)_2$	0.804	302.2	260.0	42.2	28.0
$B_5H_9 \cdot 3NH(C_2H_5)_2$	0.810	403.7	349.5	54.2	35.9
$B_5H_9 \cdot 4NH(C_2H_5)_2$	0.804	505.2	442.0	63.2	19.6
$B_5H_9 \cdot 5NH(C_2H_5)_2$	0.785	606.2	540.0	66.2	14.1

As the pentaborane was added a thick yellow mass accumulated in the lower part of the reaction vessel and when left to stand for 1 hour at −5° this mass became white. The excess triethylamine was distilled off in vacuo at −5° over a period of 3 hours. The temperature in the bath was not raised higher, since the solid white precipitate softened at a temperature above 0°. The distillate, collected in a receiver at a temperature of −196°, amounted to 28.6 g and proved to be pure triethylamine. 6 g pentaborane had thus reacted with 19.2 g triethylamine, which corresponds to a ratio of $B_5H_9 : N(C_2H_5)_3 = 1 : 2$. Experiments were carried out with component ratios of 1 : 3, 1 : 4, 2 : 1. The same results were obtained in these experiments.

c) The preparation of dimethylamine–pentaborane complexes. The preparation of $B_5H_9 \cdot 2NH(CH_3)_2$. The experiment was carried out in an apparatus similar to that shown in Figure 1, with this difference, that instead of the dropping funnel, a bulb with dry dimethylamine, flow-meter and manometer was attached.

8.9 g (0.198 mole) dimethylamine was passed through 12.6 g (0.2 mole) pentaborane, cooled to −15°, at such a rate that the temperature in the reaction mass did not exceed −3°. The dimethylamine was completely absorbed with no evolution of hydrogen and no formation of precipitate. When the calculated quantity of dimethylamine had been passed, the excess pentaborane was distilled in vacuo (1-2 mm) from the reaction liquid

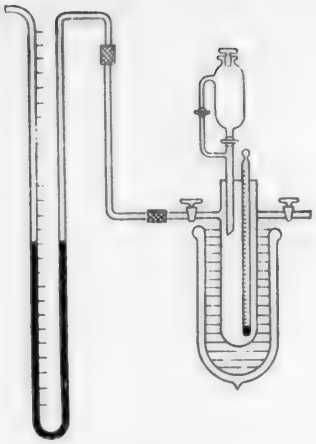

Fig. 1. Explanation in the text.

as the temperature in the bath was gradually raised from −15° to 0°. The liquid was maintained for 3 hours at 0° and for 0.5 hours at room temperature. 6.6 g (0.104 mole) of distillate, collected in a receiver at a temperature of −196°, proved to be pure pentaborane. 6 g (0.095 mole) of pentaborane and all the dimethylamine had thus reacted, which corresponds to a ratio $B_5H_9 : NH(CH_3)_2 = 1 : 2$.

The other complexes of dimethylamine and pentaborane were prepared in similar fashion, the proportions of the starting materials being the same as in the reaction with diethylamine (see above). The data on the complexes obtained are given in Table 1.

d) The preparation of trimethylamine–pentaborane complexes. The preparation of $B_5H_9 \cdot 2N(CH_3)_3$. The experiment was carried out in the apparatus used for the reaction with dimethylamine. The component ratio taken for the reaction was $B_5H_9 : N(CH_3)_3 = 1 : 5$. 4 g pentaborane was added with cooling to −20° and shaking to 18.5 g trimethylamine condensed to a given mark. The temperature in the reaction mass showed no sharp rise and no hydrogen was evolved. As the pentaborane was added a white precipitate formed. The reaction mass was left for 1 hour at −5° and the excess trimethylamine distilled off in vacuo at this temperature. The distillate, collected in a receiver at a temperature of −196°, amounted to 11 g and proved to be pure trimethylamine. All the pentaborane had thus reacted with 7.5 g trimethylamine. This corresponds to a ratio of $B_5H_9 : N(CH_3)_3 = 1 : 2$.

e) The properties of the complex compounds. The complexes formed by the secondary amines with pentaborane are transparent liquids, non-volatile in vacuo, and have a specific sharp odor which is not like the odor of pentaborane. The complexes $B_5H_9 \cdot 2NH(C_2H_5)_2$ and $B_5H_9 \cdot 2NH(CH_3)_2$ solidify to a white mass when cooled to −55 to −60°, while the other complexes obtained form a glass at the same temperature. The complexes become soft when heated and become mobile at room temperature. The specific gravities of the complex compounds were measured using a pyknometer and their viscosities determined using an Ostwald apparatus. The determinations were carried out in an atmosphere of purified nitrogen (Table 2).

The complexes formed by the tertiary amines with pentaborane are solid white substances which are less stable to heat than the complexes formed by the secondary amines, and are completely decomposed at room temperature.

All the complexes obtained are soluble in benzene, petroleum and pentaborane. The solution have a low stability at room temperature. The complexes are not spontaneously inflammable in air but catch fire when dropped on cotton wool or cloth. The complexes with the tertiary amines are more reactive and swell up rapidly on mere contact with moist air and catch fire when water is dropped in.

The hydrolysis of the complexes by water takes place vigorously (particularly in the case of the complexes with the tertiary amines) with the formation of an oily layer of composition BH_2NR_2 and BH_3NR_3 which undergoes further slow hydrolysis at room temperature over a period of many hours. Boiling with dilute hydrochloric acid leads to quantitative hydrolysis with the formation of hydrogen, boric acid and the amine salt according to the equation.

$$B_5H_9 \cdot 2NHR_2 + 2HCl + 15H_2O \rightarrow 5B(OH)_3 + 2NHR_2 \cdot HCl + 12H_2$$

The reaction given was made the basis of a method for the determination of boron in the complexes described, in the form of boric acid.

The complexes react with acetone with the evolution of heat and the formation of a white precipitate; they react with methyl and ethyl alcohols with the liberation of hydrogen.

II. Thermal decomposition of the amine–pentaborane complexes

As has been pointed out, heating of the complexes above room temperature brings about their decomposition with the formation of alkylamino derivatives of diborane, borine and hydrogen.

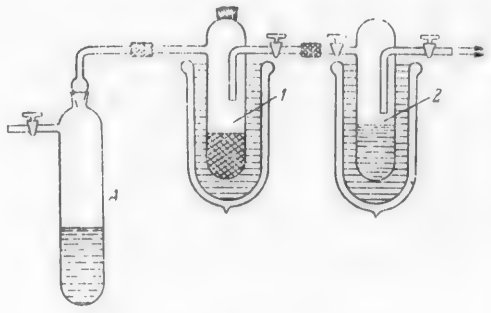

Fig. 2. Explanation in text.

a) The decomposition of the diethylamine–pentaborane complexes. The heat treatment of the complex $B_5H_9 \cdot 2NH(C_2H_5)_2$ was carried out in an apparatus consisting of a reaction vessel (A) of elongated shape and two receivers (1) and (2) (Figure 2).

11.4 g of the complex was placed in the vessel (A), which was then immersed in an oil bath to the level of the liquid contained in the vessel, gas burets were connected to the receiver (2), and as the hydrogen was liberated the temperature in the bath was raised to 100-120°. The reaction mass was maintained at this temperature for 1.5-2 hours until the evolution of hydrogen was complete. The solution acquired a yellow color and a precipitate was obtained. The volume of hydrogen evolved was measured, the gas burets disconnected, the vessel (A) lowered into the bath to the level of the outlet tubes so that crystals would not form on the walls of the vessel, and the apparatus connected to a vacuum pump.

The reaction products were separated by fractional condensation, for which the vessel (A) was heated gradually to 120° and the vapors passed through the receivers, which were cooled to temperatures of −10° in the 1st and −196° in the 2nd.

A white solid substance, whose composition corresponded to that of diethylaminoborine dimer, condensed in the first receiver.

Found %: B 12.9; N 16.3; H 14.6; C 57.0. M 168.7. $[BH_2N(C_2H_5)_2]_2$. Calculated %: B 12.74; N 16.5; H 14.25; C 56.5. M 169.7.

Diethylaminoborine sublimes readily on slight heating or on prolonged storage at room temperature in the form of beautiful long crystals with m.p. 47°. Diethylaminoborine is a stable compound. The substance underwent no change after storage for 1 year in an atmosphere of air. It undergoes practically no hydrolysis with water at room temperature; hydrolysis takes place quantitatively on boiling with dilute hydrochloric acid. The substance is readily soluble in benzene, ether, acetone, methyl and ethyl alcohols, diethylamine, pentaborane and diethylamonodiborane. Diethylaminoborine is described in detail for the first time. The literature [6] only indicates that this substance sublimes in vacuo at 45-50°.

A substance whose composition corresponded to that of diethylaminodiborane condensed in the second receiver. The substance is described for the first time: m.p. −64°, b.p. 105.8 (760 mm), d_4^{20} 0.703.

Found %: B 21.85; N 14.3; C 48.3; H 15.3. M 99.6. $B_2H_5N(C_2H_5)_2$. Calculated %: B 21.92; N 14.18; C 48.6; H 15.3. M 98.9.

Diethylaminodiborane is a colorless, transparent, very mobile liquid which distils completely without decomposition and dissolves readily in benzene, petroleum, ether, pentaborane. It is miscible with diethylaminoborine forming transparent solutions which distil leaving no residue. The boiling point of such solutions depends on the ratio of the components $B_2H_5N(C_2H_5)_2$ and $BH_2N(C_2H_5)_2$ taken, and varies between 90 and 105°. The greater the diethylaminoborine content, the lower the boiling point of the solution. This property may be used for the separation of a mixture of the compounds $B_2H_5N(C_2H_5)_2$ + $BH_2N(C_2H_5)_2$ from polymers by distillation of this mixture from a Claisen flask. Diethylaminodiborane is readily distilled in vacuo from diethylaminoborine at room temperature, since in these conditions the diethylaminoborine is nonvolatile.

TABLE 3

Thermal Decomposition of the Complexes $B_5H_9 \cdot nNHR_2$ (R = C_2H_5 or CH_3)

Composition of complex	Amount of complex (in moles)	Amount of decomposition products				Per 1 mole original complex (moles)		
		BH_2NR_2 (moles)	$B_2H_5NR_2$ (moles)	H_2 (moles)	polymer (g)	BH_2NR_2	$B_2H_5NR_2$	H_2
$B_5H_9 \cdot 2NH(C_2H_5)_2$	0.0545	0.0236	0.0758	0.0206	1.6	0.43	1.39	0.38
$B_5H_9 \cdot 3NH(C_2H_5)_2$	0.0368	0.0377	0.0707	—	Traces	1.02	1.91	—
$B_5H_9 \cdot 4NH(C_2H_5)_2$	0.0208	0.0613	0.0213	0.0199	Traces	2.94	1.0	0.94
$B_5H_9 \cdot 5NH(C_2H_5)_2$	0.0135	0.0648	—	0.0259	—	4.80	—	1.91
$B_5H_9 \cdot 2NH(CH_3)_2$	0.077	0.030	0.108	0.0284	2.0	0.39	1.40	0.37
$B_5H_9 \cdot 3NH(CH_3)_2$	0.0534	0.0475	0.102	0.005	0.4	0.9	1.9	0.09
$B_5H_9 \cdot 4NH(CH_3)_2$	0.048	0.134	0.0467	0.043	0.3	2.8	0.97	0.9
$B_5H_9 \cdot 5NH(CH_3)_2$	0.053	0.255	—	0.108	Traces	4.75		2.0

Diethylaminodiborane is not spontaneously inflammable in air, but a gelatinous precipitate is formed when the substance is left to stand in an open vessel. Hydrolysis by water takes place over a period of many hours. Hydrolysis takes place rapidly and quantitatively when the substance is boiled with 0.5 N HCl. It reacts with acetone and ethyl alcohol with the evolution of hydrogen.

The residue in the flask formed a yellow solid mass – a polymer. A study of the polymer showed that it is made up of B, H, C and N. The polymer evolves no volatile products when heated in vacuo to 150°. The quantities of decomposition products obtained are given in Table 3. It can be seen from these data that the thermal decomposition of the complex is described by Equation (1) (see above). The experiments with the other complexes of B_5H_9 and diethylamine were carried out in analogous fashion. The data are given in Table 3.

b) The decomposition of $B_5H_9 \cdot 2N(C_2H_5)_3$. The thermal decomposition of the complex was carried out in the same vessel in which it had been prepared, since the extremely solid nature of the complex made it difficult to extract from the reaction vessel. The complex was heated to 25-30°, at which temperature decomposition took place accompanied by the evolution of heat. When left to stand for 2-3 hours the reaction mass liquified and two layers were formed: the upper layer a yellow-colored liquid, the lower layer a fine yellowish precipitate. . The decomposition process took place with no evolution of hydrogen. The reaction mass was shaken and transferred for distillation to an apparatus consisting of a Claisen flask, condenser and receiver. The apparatus was connected to a vacuum pump and the flask gradually heated at 5-7 mm first of all to 100° and, towards the end of the distillation, to 120°. The liquid distillate came over completely at 86° (7 mm) on a second distillation. The substance obtained corresponded in molecular weight and analysis results to triethylaminoborine, which is described for the first time, m.p. –4°, d_4^{20} 0.785.

Found %: B 9.2; N 12.0; C 62.9; H 15.35. M 114.7. $BH_3N(C_2H_5)_3$. Calculated %: B 9.41; N 12.18; C 62.6; H 15.77. M 115.0.

Triethylaminoborine is a colorless, transparent, very mobile liquid with an odor of pine needles. It dissolved readily in benzene, ether, pentaborane and triethylamine. It is not spontaneously inflammable in air, but a gelatinous precipitate is formed when the substance is left to stand. It is quite stable in the absence of air and may be heated without noticeable decompositon up to 100°, but begins to decompose above this temperature. At room temperature practically no hydrolysis but water takes place, but it is completely hydrolyzed when boiled with 0.5 N HCl.

The residue in the distillation flask formed a solid yellow mass – a polymer, containing B, H, N and C. The products obtained as the result of the reaction starting with 18.6 g (0.07 mole) complex were: $BH_3N(C_2H_5)_3$ – 11.5 g (0.1 mole), polymer – 6.5 g. The experimental data obtained correspond to equation (5).

c) The decomposition of the dimethylamine – pentaborane complexes was carried out in the same way as in the case of the diethylamine complexes. 11.8 g (0.077 mole) of the complex $B_5H_9 \cdot 2NH(CH_3)_2$ was taken. As the vessel (A) (Figure 2) was heated to 100°, the solution became turbid, a fine white precipitate came down and hydrogen was evolved. Towards the end of the experiment the reaction mass became viscous. Separation of the mass was achieved by fractional condensation in vacuo. The vapor was passed through the receivers cooled to temperatures of −30° for the first reveiver and −196° for the second (Figure 2). A white solid substance (m.p. 74°), which proved to be pure dimethylaminoborine, condensed in the left-hand receiver [1, 6].

Found %: B 18.8; N 24.35; C 41.5; H 14.0. M 112.80. $[BH_2N(CH_3)_2]_2$. Calculated %: B 19.03; N 24.65; C 42.2; H 14.15. M 113.66.

A substance corresponding in composition to dimethylaminodiborane [1], condensed in the second receiver. M.p. −54°; b.p. 51°.

Found %: B 30.8; N 19.3; C 33.1; H 15.38. M 71.4. $B_2H_5N(CH_3)_2$. Calculated %: B 30.6; N 19.8; C 33.94; H 15.68. M 70.7.

The residue in the distillation flask formed a solid yellow mass – a polymer containing B, H, N and C.

The other dimethylamine complexes were studied in analogous fashion. The results are given in Table 3.

d) The decomposition of $B_5H_9 \cdot 2N(CH_3)_3$. 8.0 g of the complex was placed in an apparatus for distillation and heated gradually to 120°; in the process, the complex liquefied and transparent needle-shaped crystals sublimed. As the heating continued, the reaction mass diminished, while the amount of crystals formed on the inner tube of the apparatus increased. The process was complete in 2 hours. Decomposition took place with no evolution of hydrogen. A solid yellow mass – polymer $(BH)_x$ and amine – remained in the apparatus.

The crystalline substance obtained, with m.p. 94°, proved from our experimental data to be trimethylaminoborine [4].

Found %: B 15.0; N 19.3; C 49.9; H 16.9. M 73.9. $BH_3N(CH_3)_3$. Calculated %: B 14.48; N 19.2; C 49.37; H 16.5. M 72.9.

The products obtained from the reaction were: $BH_3N(CH_3)_3$ – 4.42 g (0.06 mole), polymer – 3.4 g. The experimental data obtained correspond to equation (5).

III. The reaction of diethylaminodiborane with diethylamine

As has been mentioned earlier, diethylaminodiborane reacts with diethylamine with the formation of the addition product $B_2H_5N(C_2H_5)_2 \cdot NH(C_2H_5)_2$. The experiment was carried out in the apparatus shown in Figure 1. 8.6 g (0.087 mole) diethylaminodiborane was placed in the reaction vessel and after first cooling to −20°, 3.2 g (0.087 mole) diethylamine was added with shaking from the dropping funnel. The reaction took place with considerable evolution of heat. No hydrogen was evolved. The temperature in the reaction solution was controlled by the rate of addition of diethylamine and was maintained below −5°. The liquid obtained was not volatile in vacuo.

Found %: B 12.30; N 16.0. $B_2H_5N(C_2H_5)_2 \cdot NH(C_2H_5)_2$. Calculated %: B 12.65; N 16.10.

The thermal decompositon of $B_2H_5N(C_2H_5)_2 \cdot NH(C_2H_5)_2$ was carried out in the special apparatus (Figure 2). 6.5 g (0.037 mole) of the complex was boiled until the evolution of hydrogen ceased, the solution was cooled and seeded with some crystals of diethylaminoborane; the solution solidified. The product was transferred to an apparatus for distillation and heated to 40-45° at atmospheric pressure to distil off crystals corresponding in molecular weight and analysis results to diethylaminoborine. Yield 93% of theoretical. Products formed in the reaction: $BH_2N(C_2H_5)_2$ – 5.9 g (0.069 mole), H_2 – 800 ml (0.0358 mole), polymer – 0.4 g. From the data obtained we may write the following equation

$$B_2H_5N(C_2H_5)_2 \cdot NH(C_2H_5)_2 \rightarrow 1.86BH_2N(C_2H_5)_2 + 0.96H_2 + \text{polymer}$$

SUMMARY

1. A study has been made of the reactions of pentaborane with dimethyl-, diethyl-, trimethyl and triethylamine. It has been established that the primary reaction at low temperatures (up to 0°) leads to the direct addition

of the amine to the pentaborane with the formation of complex compounds of the type $B_5H_9 \cdot nNHR_2$, where n = 2, 3. 4, 5 in the case of the secondary amines, and of the type $B_5H_9 \cdot 2NR_3$ for the tertiary amines.

2. As the temperature is increased, decomposition of the complexes takes place with the evolution of hydrogen, breakdown of the pentaborane molecule and formation of alkylamino derivatives of diborane and borine. Equations have been given for the main reactions of thermal decomposition of the pentaborane–alkylamine complexes.

3. A number of pentaborane complexes and derivatives of diborane and borine have been prepared and characterized.

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SPATIAL CONFIGURATION AND REACTIVITY

VIII. ON THE INTERACTION OF SUBSTITUENT GROUPS ACROSS TWO BENZENE RINGS BRIDGED BY A SULFUR ATOM, FROM INVESTIGATIONS OF THE KINETICS OF ACYLATION OF 4-AMINO- AND 4-AMINO-4'-NITRODIPHENYL SULFIDE

L. M. Litvinenko, S. B. Tsukerman, R. S. Cheshko, and B. M. Kolesnikova

In the previous communication [1] we have shown that the interaction of the NO_2 and NH_2 groups (in positions 4 and 4') across the molecule of diphenyl oxide takes place with as much energy as it does in the case of diphenyl, although in the former case the two benzene rings are separated by the oxygen atom while in the case of diphenyl they are linked directly with each other. We have thus demonstrated that the effect of increased distance between the NO_2 and the NH_2 groups in the case of derivatives of diphenyl oxide, as compared with this distance in similar derivatives of diphenyl, is compensated or perhaps even masked by some other factor which facilitates electronic interaction between these substituents across two benzene rings linked by an oxygen atom, i. e., in spite of the fact that in this system we no longer have, like in diphenyl, a continuous chain of conjugated double bonds. This conclusion was arrived at on the basis of results obtained from the investigation of the kinetics of acylation of 4-amino and 4-amino-4'-nitrodiphenyl oxide with p-nitrobenzoyl chloride in benzene solution. In order to develop these ideas further we report in the present paper data from the investigation of the kinetics of acylation of sulfur-containing compounds of the same type, namely, 4-amino- and 4-amino-4'-nitrodiphenyl sulfide, under conditions identical with those used in previous investigations.

EXPERIMENTAL

I. Purification of reagents. Benzoyl chloride and p-nitrobenzoyl chloride were purified as described previously [2]. After preliminary purification the amines were recrystallized several times from solvents which were specially purified for this purpose, until the melting points were constant as indicated below.

II. Preparation of the amines. 4-Aminodiphenyl sulfide. This was prepared from benzoylsulfinic acid [3] and aniline chloride by the method of Hinsberg [4]. The amine was then recrystallized by the following sequence of operations: twice recrystallized from dilute (2:1) methanol, followed by one recrystallization as the hydrochloride from dilute hydrochloric acid (1:1), and was finally recrystallized four times from a mixture of equal volumes of water, concentrated hydrochloric and glacial acetic acids (the first two recrystallizations were done in the presence of charcoal). The hydrochloride was decomposed with aqueous ammonia and the free amine was recrystallized again three times from aqueous methanol (1:1). The amine thus obtained was dried in vacuo at 65°. M.p. 96-97°; literature [5], 96°.

4-Amino-4'-nitrodiphenyl sulfide. To a gently boiling solution of 7 g of 4,4'-dinitrodiphenyl sulfide [6] in 90 ml of acetone was added dropwise, over 15 minutes, 54 ml of a molar acetone-aqueous solution of sodium disulfide [1]. After all of the reducing agent was added boiling under reflux was continued for 20 minutes and the solution was then acidified with hydrochloric acid (preferably concentrated) (Congo red). The liquid was evaporated almost to dryness and the amine was extracted from the residue with 50 ml portions of dilute (1:1) hydrochloric acid until the crystalline precipitate of the hydrochloride could no longer be obtained from the cooled solution. The combined extracts were treated with active charcoal. The hydrochloride was once more recrystallized from hydrochloric acid of the same concentration; yield, 3.4 g (48%). To purify the hydrochloride

TABLE 1

Kinetics of the Acylation of 4-Aminodiphenyl Sulfide with p-Nitrobenzoyl Chloride (a = 0.0925 mole/liter, b = 0.005 mole/liter)

25°				50°			
t_i Min.)	Yield (%)	$\bar{k}_i$ (1/mole × sec)	n_i	t_i (min.)	Yield (%)	$\bar{k}_i$ (1/mole × sec)	n_i
4	12.4	0.118	2	3	20.5	0.296	5
10	25.0	0.112	3	5	27.9	0.268	3
20	39.8	0.111	3	8	41.7	0.308	3
37	60.4	0.138	3	20	64.4	0.312	4
71	72.1	0.122	3	30	73.4	0.317	2
$k_{25} = 0.120 \pm 0.006$				$k_{50} = 0.300 \pm 0.012$			

E = 7000 cal/mole; PZ = $1.70 \cdot 10^4$ liter/mole·sec; $\Delta S^{\#}$ = −41.2 cal/deg·mole

TABLE 2

Kinetics of the Acylation of 4-Amino-4'-nitrodiphenyl Sulfide with p-Nitrobenzoyl Chloride (a = 0.0025 mole/liter; b = 0.005 mole/liter)

25°				50°			
t_i (min.)	Yield (%)	$\bar{k}_i$ (1/mole × sec)	n_i	t_i (min.)	Yield (%)	$\bar{k}_i$ (1/mole × sec)	n_i
77	10.7	0.00522	2	20	10.0	0.0193	3
120	15.6	0.00518	4	60	23.3	0.0175	3
230	24.4	0.00470	3	125	38.5	0.0173	3
460	39.2	0.00470	3	230	51.9	0.0169	3
720	52.1	0.00506	2	440	70.5	0.0188	3
1020	62.2	0.00541	3				
$k_{25} = 0.00504 \pm 0.00018$				$k_{50} = 0.0178 \pm 0.0008$			

E = 9700 cal/mole; PZ = $6.3 \cdot 10^4$ liter/mole·sec; $\Delta S^{\#}$ = −38.5 cal/deg·mole

TABLE 3

Collected Data on the Kinetics of Acylation of Amines with p-Nitrobenzoyl Chloride *

Amine	K_{25}	K_{50}	E	PZ	$\Delta S^{\#}$
$C_6H_5-O-C_6H_4-NH_2$-n[1] . . .	1.23±0.03	2.60±0.11	5550	$1.49 \cdot 10^4$	−41.5
n-$NO_2-C_6H_4-O-C_6H_4-NH_2$-$n$[1]	0.102±0.003	0.273±0.006	7500	$3.4 \cdot 10^4$	−39.9
$C_6H_5-S-C_6H_4-NH_2$-n	0.120±0.006	0.300±0.012	7000	$1.70 \cdot 10^4$	−41.2
n-$NO_2-C_6H_4-S-C_6H_4-NH_2$-$n$ [9]	0.00504±0.00018	0.0178±0.0008	9700	$6.3 \cdot 10^4$	−38.5
$C_6H_5-C_6H_4-NH_2$ [9]	0.533±0.010	1.11±0.02	5600	$7.1 \cdot 10^3$	−42.8
n-$NO_2-C_6H_4-C_6H_4-NH_2$-n [9] .	0.0505±0.0011	0.118±0.003	6500	$2.9 \cdot 10^3$	−44.7
$C_6H_5-NH_2$ [7]	0.580±0.018	—	—	—	—

* The dimensions of the various quantities are the same as those in Tables 1 and 2.

further it was recrystallized three times with dilute hydrochloric acid (3 : 2). The free amine was obtained by decomposing the hydrochloride with aqueous ammonia followed by recrystallizing twice from toluene and methanol, finally once from benzene. After drying at 100° in vacuo the amine had a melting point of 144-145° which is in agreement with literature data [5].

III. The determination of reaction rates and the results. The method used in the determination of rates of reaction has been described in detail in one of our previous communications [7]. It consisted of adding to the reaction mixture at a given time a benzene solution of diethylamine, thereby stopping the reaction and determining the nonacylated amine by potentiometric titration with sodium nitrite [8].

The initial concentration of benzoyl chloride (a) in each experiment was equal to half the initial concentration of the amine (b). The calculation of the bimolecular velocity constant, energy of activation (E), the preexponential term of the Arrhenius equation (PZ) and of the entropy of activation ($\Delta S^{\#}$) was carried out in exactly the same manner as already described [7].

The numerical data obtained for the reactions investigated in the present work are given in Tables 1 and 2 where the various symbols have the following meaning: t_i is the time intervals at the end of which reaction velocity was determined, k_i and $\underline{k}$ are the mean values of the velocity constants, respectively, for a given value of t_i for n_i measurements and for Σn_i measurements. The second column gives the mean yield of the reaction products obtained in n_i determinations.

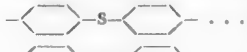
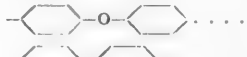
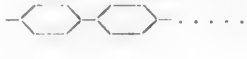
In Table 3 are listed the fundamental data on the kinetics of the reactions described in the present work as well as the values of some of these quantities in the case of reactions studied previously [1, 9].

DISCUSSION OF RESULTS

The results summarized in Table 3 indicate that, unlike the C_6H_5O- group which possesses electron-donating characteristics [1], or the phenyl group which is nearly electrically neutral [2, 9], the C_6H_5S- group placed in the para position in aniline exhibits a distinct electron-accepting character; this is evident from the fact that the velocity constant of acetylation decreases by nearly 5 times as we pass from aniline to 4-aminodiphenyl sulfide.

TABLE 4

Factors f for Molecular Systems of Diphenyl Sulfide, Diphenyl Oxide and Diphenyl

System	f_{25}°
	23.8
	12.1
	10.6

As we have already pointed out [10], a convenient quantitative index of the energy of electronic interaction between two substituents situated at opposite ends of a molecular system similar to those under consideration, may be obtained from the ratio of the reaction velocity constant of the mono- to that of the disubstituted compound (factor f); for example, in the case of the diphenyl sulfide system this would be given by the ratio of the acetylation velocity constants of 4-amino- and 4-amino-4'-nitrodiphenyl sulfides. In the latter case the value of this factor ($f_{25°} = 23.8$) shows that the diphenyl sulfide molecule transmits efficiently the interaction between the NO_2 and the NH_2 groups. From a comparison of the value of f for this system with its values for the systems of diphenyl oxide and diphenyl (Table 4) it will be seen that the three molecular systems can be placed in the order: diphenyl sulfide > diphenyl oxide ≥ diphenyl, with regard to their ability to assist electronic interaction between constituents in the two rings. We may, therefore, conclude that the introduction of an atom of oxygen or sulfur between the two benzene rings of the diphenyl molecule, whereby the direct link between the rings is broken and the conjugated system disturbed, results not in a weakening but, in fact, in a strengthening of the interaction of the NO_2 and NH_2 groups in 4,4'-positions. This will be seen from the fact that the diphenyl oxide system is at least equal to diphenyl as a transmitter of electronic interactions between the substituents, while the diphenyl sulfide molecule is considerably better in this respect.

In order to explain this phenomenon we shall, for the time being, refer the reader to the results and theories discussed in our previous communication [1]. We may only add that the more effective transmission of electronic interactions in the diphenyl sulfide system as compared with the diphenyloxide system may be taken as a further proof of the very real significance of p,π-conjugation* in the benzene rings through the interlinking oxygen or sulfur atoms; this concept may help in understanding the characteristic features of the molecular systems under consideration. In actual fact, the interaction of the unoccupied p-electrons of the sulfur atom with the benzene rings in diphenyl sulfide will be more energetic than in the case of similar electrons of the oxygen atom in diphenyl oxide: in accordance with the position of sulfur in the Periodic Table the p-electrons of the sulfur atom should be more mobile and, therefore, enter more easily into conjugation with electrons forming double bonds.

* For definition of this concept see [11].

Speaking in terms of the energetics of reactions, the acylation of 4-aminodiphenyl sulfides and 4-amino-4'-nitrodiphenyl sulfide with p-nitrobenzoyl chloride may be characterized by the fact that the energies of activation of both reactions are somewhat higher than the values for the corresponding reactions of aminonitro-derivatives of diphenyl oxide [1]. On the other hand, the entropies of activation of the acylation of both pairs of derivatives are practically identical.

SUMMARY

1. The kinetics of acylation of 4-aminodiphenyl sulfide and 4-amino-4'-nitrodiphenyl sulfide with p-nitrobenzoyl chloride in benzene has been investigated.

2. It has been shown that the molecule of diphenyl sulfide transmits with greater ease the electronic interaction between substituent groups situated in the two benzene rings than does the molecule of diphenyl, even though in diphenyl sulfide the two rings are separated by a sulfur "bridge" while in diphenyl they are linked directly.

3. The sulfur atom linking the two benzene rings transmits electronic interactions across the molecule with greater ease than does the oxygen atom in this position.

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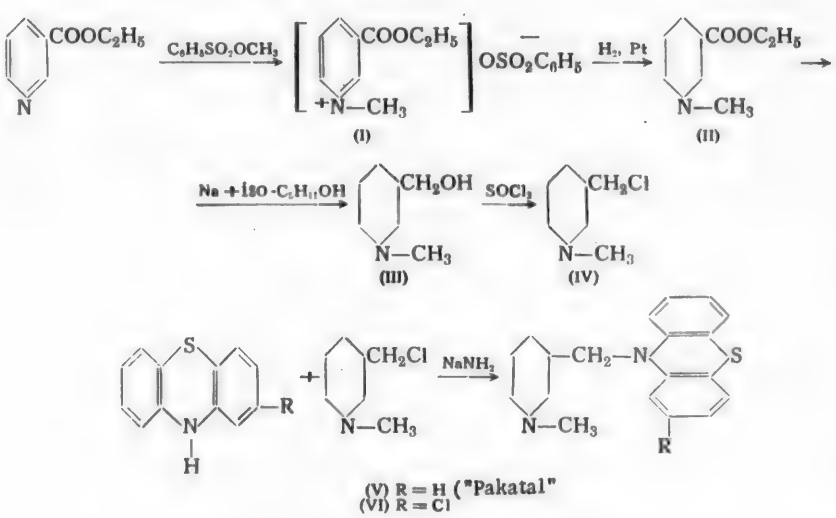
SYNTHESIS IN THE PHENOTHIAZINE SERIES

II. SYNTHESIS OF 10-(N-METHYLPIPERDYL-3-METHYL)PHENOTHIAZINES

S. V. Zhuravlev, A. N. Gritsenko, and M. I. Dorokhova

Recently reports have appeared in the literature describing trials with derivatives of N-alkylpiperidylphenothiazine among which the proprietary preparation P-391 – containing 10-(N-methylpiperidyl-3-methyl)phenothiazine – was found to have some very interesting properties [1]. Under the name of "Pakatal" this preparation was tested clinically. The authors of [1] consider that the compound may be used to stabilize blood pressure in major operations as well as in operations necessitating artifical lowering of the body temperature; it is also indicated as a soporific in mental and other disorders. No data on the method of preparation or the properties of this compound are available in the literature.

With the view of investigating the pharmacological properties of this interesting compound we have accomplished its synthesis by the following scheme:



Concurrently with our studies on "Pakatal" we have also prepared another derivative of this series, namely 10-(N-methylpiperidyl-3-methyl)-2-chlorophenothiazine, (VI) by condensation of 2-chlorophenothiazine with 3-chloromethyl-N-methylpiperidine (IV).

The latter compound (IV) has been described by Feldkamp, Faust and Cushman [2]. They prepared this compound from ethyl nicotinate which they reduced first over a platinum oxide catalyst and subsequently over a palladium catalyst, using high pressures, and thus obtained the ethyl ester of N-methylhexahydronicotinic acid. The latter was then transformed into N-methylpiperidyl-3-carbinol by reduction with sodium and 4-methylpentanol-2 in toluene; the carbinol was then changed into the chloride by interaction with thionyl chloride. We have

used essentially the method of Feldkamp; however, we have shown that it is possible to avoid the high pressures in the preparation of the ethyl ester of N-methylhexahydronicotinic acid if the reduction is carried out not with the ester itself but with its quaternary salt with methyl benzenesulfonate (I). In the preparation of N-methylpiperidyl-3-carbinol (III) it was also found possible to replace 4-methylpentanol-2 by the more accessible isoamyl alcohol. The constants of the compounds obtained by us are in agreement with the data reported by Feldkamp.

In order to prepare 10-(N-methylpiperidyl-3-methyl)phenothiazines we used the method of Gilman and co-workers [3] intended by these authors for the preparation of 10-alkylphenothiazines, i. e., by the condensation of the corresponding alkylpiperidyl halides with phenothiazine in the presence of sodamide in liquid ammonia or in an indifferent solvent. However, the interaction between 3-chloromethyl-N-methylpiperidine and phenothiazine in the presence of sodamide which was prepared from metallic sodium in liquid ammonia, proceeded smoothly only when the ammonia was evaporated and the residue kept at 140° for 3-4 hours.

The compounds prepared are being examined in the Department of Pharmacology by Yu. I. Vikhlyaev. Preliminary trials with 10-(N-methylpiperidyl-3-methyl)phenothiazine which we have named "Mepazine," have shown that its action is similar to that of the preparation "Pakatal" described in the literature. The introduction into the aromatic nucleus of a chlorine atom weakens the antihistaminic activity and enhances the narcotic activity of the substances.

EXPERIMENTAL

The ethyl ester of N-methylhexahydronicotinic acid (II). Into a round-bottom flask provided with a reflux condenser carrying a calcium chloride tube, was placed 16.6 g of ethyl nicotinate, 18.9 g of methyl benzenesulfonate and 25 ml of dry acetone. The mixture was heated on a water bath during 2-2.5 hours. After cooling was added 25 ml dry ether and the residue which separated was filtered off, and dried in a desiccator. The quaternary salt of methyl benzosulfonate of ethyl nicotinate was obtained as colorless plates, yield 33.5 g (94.5 %). The crystals deliquesce on exposure to air; the melting point of the substance in a sealed capillary was 72-74°. The substance dissolves easily in alcohol, water and in hot acetone and is insoluble in ether.

Found %: N 4.05, 4.39; C 55.95, 55.94; H 5.49, 5.39. $C_{15}H_{17}NO_5S$. Calculated %: N 4.33; C 55.71; H 5.29.

129.6 g of the quaternary salt was dissolved in 280 ml of ethyl alcohol. To the solution was added 0.4 g of platinum oxide and the substance was hydrogenated in a hydrogenation apparatus at atmospheric pressure. The absorption of the theoretical amount of hydrogen (26.8 liters) required 8-12 hours. The catalyst was filtered off, the alcohol was removed from the filtrate and the residue was treated with 40% potassium hydroxide until alkaline to phenolphthalein. The precipitate which formed was filtered off and washed several times with ether. The ether extracts were combined and dried over sodium sulfate. Ether was removed and the residue distilled in vacuo. There was obtained 52.45 g (76.5%) of the methyl ester of N-methylhexahydronicotinic acid, b. p. 92-93° at 15.5 mm; n_D^{22} 1.4490.

N-Methylpiperidyl-3-carbinol (III). Into a three-necked flask provided with a stirrer, reflux condenser carrying a $CaCl_2$-tube, and a dropping funnel, was placed 400 ml of toluene and 52.5 g of metallic sodium. The flask was placed in an oil bath and the mixture was heated to refluxing when the stirrer was started dispersing the molten sodium into fine droplets. To the well-stirred and continuously boiling toluene was added, over 3-4 hours, a mixture consisting of 94.2 g of the methyl ester of N-methylhexahydronicotinic acid, 100 g of isoamyl alcohol and 165 ml of toluene. The mixture was kept under reflux for 30 minutes, cooled to 80-90° and diluted carefully with 75 ml of water. The flask was then placed on a water bath and heated for 1 hour. In order to achieve complete decomposition the contents were allowed to stand overnight. Toluene was removed and the aqueous layer was extracted twice with toluene. The extracts were combined and dried over magnesium sulfate. Toluene was removed, followed by removal of isoamyl alcohol in vacuo, and the residue was distilled. There was obtained 61.6 g (86.9%) of N-methylpiperidyl-3-carbinol, b. p. 109-111° at 15 mm, n_D^{17} 1.4760.

Found %: N 10.57. $C_7H_{15}NO$. Calculated %: N 10.82.

3-Chloromethyl-N-methylpiperidine (IV). 103 g of (III) was dissolved in 410 ml of dry chloroform and the solution was saturated with dry hydrogen chloride until two distinct layers formed. To the reaction mixture was

added gradually 156 ml of thionyl chloride and the contents were refluxed on a water bath for two hours. The solvent was then removed and alcohol was added to the dry residue. The latter was again removed, the operation being repeated twice, the crystalline residue was dissolved in a minimum of alcohol, cooled and diluted with absolute ether. The precipitate which formed was filtered off, washed with ether and dried. There was obtained 134 g (91.4%) of the hydrochloride of (IV) in the form of white crystals melting at 168-169°.

Found %: N 7.88, 7.78; Cl (total) 38.01, 38.11; Cl (ionizable) 19.21, 19.14. $C_7H_{14}NCl \cdot HCl$. Calculated %: N 7.60; Cl (total) 38.50; Cl (ionizable) 19.25.

In order to liberate the base, 70 g of the hydrochloride was dissolved in a minimum amount of water, 80 ml of ether was added and the solution was made alkaline (phenolphthalein) with 20% sodium hydroxide. Ether was removed and the aqueous solution was extracted twice with ether. The ether extracts were combined, dried over magnesium sulfate, the ether removed and the residue distilled in vacuo. There was obtained 53 g of (IV), b. p. 58-60° at 7 mm, $n_D^{19.5}$ 1.4722. Yield of the free base, 94% (calculated on the hydrochloride).

Found %: Cl 23.70; C 57.02, 56.98; H 9.67, 9.76. $C_7H_{14}NCl$. Calculated %: Cl 24.01; C 56.93; H 9.56.

10-(3-Methyl-N-methylpiperidyl)-phenothiazine (V). A 250-ml round-bottom 3-necked flask provided with a mercury-sealed stirrer with a side arm connected to a water pump, was placed in a cooling mixture of methanol and carbon dioxide. One neck carried a tube which reached to the bottom of the flask and was connected to a Tishchenko flask containing sulfuric acid and carrying a soda-lime tube. Into the flask was placed 0.1 g of ferrous nitrate, 200 ml of liquid ammonia and 0.3 g of metallic sodium. A slow current of air was drawn through the stirred reaction mixture for one hour. The air current was then shut off and the side arm connected to a soda-lime column. The tube dipping into the reaction mixture was replaced by a stopper. Another 1.4 g of metallic sodium (i. e., a total of 1.7 g) was added to the contents and the whole was stirred for 1 hour. To the fine suspension of sodamide in liquid ammonia obtained in this way [4] was added 12.0 g of phenothiazine which after some time passed into solution with a deep red color. To this reaction mixture was added 9.0 g of (IV) and the contents were stirred without external cooling. After two hours the flask was placed in an oil bath and the ammonia was removed slowly. The side arm connected to the soda-lime column was replaced by an air condenser carrying a $CaCl_2$ tube. The bath temperature was raised to 130-140° and the reaction mixture was heated at this temperature for four hours. The solid, golden-yellow mass turned liquid after 30-40 minutes' heating and towards the end of the heating period formed a mixture of a yellow-colored oil and sodium chloride. The bath temperature was then lowered and the reaction products were refluxed for one hour with 30 ml of toluene. To the cooled solution was added 75 ml of water and the reaction mixture was then treated with 5% hydrochloric acid until acid to Congo red. Next day the precipitate was filtered off and recrystallized twice from water with charcoal. There was obtained 12.54 g of a substance melting at 175-195°. After grinding in acetone, filtering and recrystallizing from water there was obtained the hydrochloride of (V), m. p. 228-229°. Fine colorless crystalline powder, easily soluble in methanol, hot absolute alcohol and hot water; fairly soluble in cold absolute alcohol, difficultly soluble in hot acetone, ethyl acetate and cold water; insoluble in ether and benzene.

Found %: N 7.97, 8.09; Cl 10.29, 10.31. $C_{19}H_{23}N_2SCl$. Calculated %: N 8.08; Cl 10.22.

The free base (V) was liberated by treating the aqueous solution of the hydrochloride with alkali. Viscous yellow oil, b. p. 180-183° (0.5 ml), easily soluble in organic solvents, insoluble in water.

Found %: N 9.09, 9.06. $C_{19}H_{22}N_2S$. Calculated %: N 9.02.

10-(3-Methyl-N-methylpiperidyl)-2-chlorophenothiazine (VI). The preparation of sodamide in liquid ammonia and the subsequent procedure was carried out under the same conditions as described above. The reaction mixture obtained after removing liquid ammonia, was heated for three hours at 140-150°. From 14 g of 2-chlorophenothiazine (m. p. 194-196°) and 9.0 g of (IV) there was obtained, after treatment with hydrochloric acid and one recrystallization from water (with charcoal), 4.8 g of a substance melting at 145-150°. On making the acid filtrate alkaline and treating the brown precipitate with hydrochloric acid, another 3.3 g of the substance was obtained. After two recrystallizations from absolute alcohol compound (VI), m. p. 210-211°, was obtained. The substance dissolves easily in methanol, chloroform, hot absolute alcohol and hot water. It is fairly soluble in cold absolute alcohol and difficultly soluble in cold water; it is insoluble in ether.

Found %: N 7.16, 6.97; Cl (total) 18.65, 18.50; Cl (ionizable) 9.36; C 59.93, 60.10; H 5.94, 6.01. $C_{19}H_{22}N_2SCl_2$. Calculated %: N 7.35; Cl (total) 18.59; Cl (ionizable) 9.29; C 59.84; H 5.81.

The free base was obtained by treating the pure hydrochloride with alkali; m.p. 56-58°. Crystalline powder, decomposes on exposure to air, easily soluble in organic solvents, insoluble in water.

Found %: N 8.36, 8.12; Cl 9.90. $C_{19}H_{21}N_2SCl$. Calculated %: N 8.12; Cl 10.28.

SUMMARY

The synthesis and the properties of 10-(3-methyl-N-methylpiperidyl)-phenothiazine and 10-(3-methyl-N-methylpiperidyl)-2-chlorophenothiazine and of their hydrochlorides has been described.

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INTERACTION OF 2,4-DINITROCHLOROBENZENE AND 2,4-DINITROBROMOBENZENE WITH FLUORIDES

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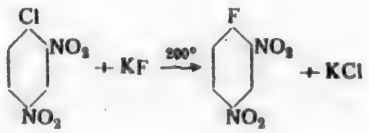
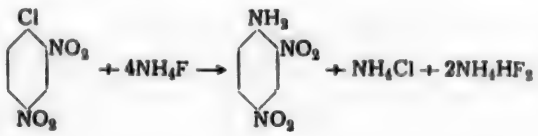
The substitution of a fluorine atom for a chlorine atom directly attached to the aromatic nucleus was accomplished successfully only in the case of 2,4-dinitrochlorobenzene [1] by prolonged heating of the latter with potassium fluoride in nitrobenzene, and in the case of picryl chloride by treatment with sodium fluoride [2]. The yields of the fluoro-derivatives were very small. For this reason 2,4-dinitrofluorobenzene which is used as a reagent for hydroxy and amino groups in proteins [3], is currently prepared by nitration of the difficultly accessible fluorobenzene.

We have now found that 2,4-dinitrofluorobenzene is formed in a yield of over 90% on heating 2,4-dinitrochlorobenzene at 200° with a slight excess of anhydrous potassium fluoride (1.1-1.3 mole) and in the absence of any solvent.

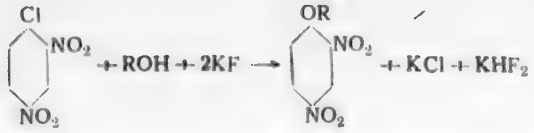


In addition there is also formed a small quantity (2-3%) of 2,2',4,4'-tetranitrodiphenyl ether. The formation of this product is of course due to the presence of moisture (0.2-0.3%) in the potassium fluoride used. The reaction between 2,4-dinitrochlorobenzene and potassium fluoride is irreversible since 2,4-dinitrofluorobenzene remains unchanged after heating for several hours with potassium chloride at 190-200°.

We have also investigated the interaction of 2,4-dinitrochlorobenzene with acid potassium fluoride, sodium fluoride and ammonium fluoride. On heating 2,4-dinitrochlorobenzene with acid potassium fluoride, 2,4-dinitrofluorobenzene was obtained in a yield of only 17%. Sodium fluoride does not react with 2,4-dinitrochlorobenzene under the conditions stated. Heating of 2,4-dinitrochlorobenzene with ammonium fluoride gives rise to the formation of 2,4-dinitroaniline in 70% yield.



The interaction between 2,4-dinitrochlorobenzene and potassium fluoride in hydroxylic media leads to the formation of esters of 2,4-dinitrophenol.



When the reaction was carried out in a nonpolar solvent – such as benzene or toluene – the yields of the esters are considerably lower. For example, the yield of the benzyl ester of 2,4-dinitrophenol is reduced from 86 to 6% when toluene is added to the reaction mixture. 2,4-Dinitrochlorobenzene does not react with alcoholic solutions of sodium fluoride or acid potassium fluoride. Under these conditions ammonium fluoride gives rise only to relatively small amounts of 2,4-dinitroaniline.

The formation of esters of 2,4-dinitrophenol is, of course, explained as being due to the fact that hydrofluoric acid is a weak acid. Therefore, in solutions of its salts with strong bases in hydroxylic solvents there will be formed alkoxy, be formed alkoxy, and correspondingly, aryloxy ions which will further react with 2,4-dinitrochlorobenzene.

$$ROH + 2F^- \rightleftarrows RO^- + HF_2^- \quad (NO_2)_2C_6H_3Cl + RO^- \rightarrow (NO_2)_2C_6H_3OR + Cl^-$$

Analogous halogen exchange reactions have also been carried out with 2,4-dinitrobromobenzene. However, the yields of 2,4-dinitrofluorobenzene and of esters of dinitrophenol are lower than in the case of 2,4-dinitrochlorobenzene, due to a slower rate of reaction. The lesser reactivity of 2,4-dinitrobromobenzene as compared with 2,4-dinitrochlorobenzene has been observed on previous occasions [4].

EXPERIMENTAL

Dehydration of potassium fluoride. Pure crystalline potassium fluoride was heated at 120-130° until the water of crystallization was removed. It was then finely ground and kept at 200° during two hours.

2,4-Dinitrofluorobenzene. Into a three-necked flask provided with a stirrer, thermometer and reflux air condenser (carrying a calcium chloride tube) was placed 30.4 g of 2,4-dinitrochlorobenzene and 10.5 g of freshly prepared anhydrous potassium fluoride. The mixture was heated for 7 hours at 190-200°. After cooling the reaction mass was treated with hot dry benzene and was filtered off from inorganic compounds. From the cooled filtrate there separated about 0.7 g (2.5%) of 2,2',4,4'-tetranitrodiphenyl ester. After recrystallization from toluene the substance melted at 194-195°. The benzene was removed and the residue distilled in vacuo through a fractionating column. B. p. 127-129° (2 mm). The yield of the product which did not contain chlorine (solidification point 21°) amounted to 25.6 g (92%). After recrystallization from methanol 2,4-dinitrofluorobenzene melting at 27° was obtained; literature, m. p. 25.8° [5].

Found %: N 14.89, 14.96. $C_6H_3O_4N_2F$. Calculated %: N 15.05.

2,4-Dinitroaniline. In a manner similar to that described above, 5.08 g of 2,4-dinitrochlorobenzene and 5 g of ammonium fluoride was heated for 5 hours at 170-180°. 2,4-Dinitroaniline was extracted from the reaction mass by the method described in [6]. Yield 2-3.4 g (66-74%), m. p. 178-179°. The acetyl derivative melts at 121°. The reaction product was identified by the absence of melting point depression in a mixture with an authentic sample of 2,4-dinitroaniline and, correspondingly, with an authentic sample of the acetyl derivative.

Esters of 2,4-dinitrophenol. The amounts of reagents used and the reaction conditions are summarized in Table 1. At the end of the reaction the mixture was treated with hot dry benzene and was separated from inorganic compounds by filtration. Benzene was removed on a water bath. The esters of 2,4-dinitrophenol were separated from unreacted dinitrochlorobenzene by fractional crystallization from methanol.

All the compounds, with the exception of n-octadecyl and phenylpropyl esters, have been described in the literature. The melting points of the esters are in agreement with literature data [7].

Interaction of 2,4-dinitrochlorobenzene with acid potassium fluoride. A mixture of 10.15 g of 2,4-dinitrochlorobenzene and 7.8 g of acid potassium fluoride was heated for 6 hours at 190-200°. 17% of 2,4-dinitrochlorobenzene reacted (as determined by titration of the chloride formed). A small amount of 2,4-dinitrofluorobenzene was isolated from the reaction mass.

TABLE 1

Interaction of 2,4-Dinitrochlorobenzene (2.03 g, 0.01 mole) with Hydroxy-Compounds in the Presence of Anhydrous Potassium Fluoride (1.16 g, 0.02 mole)

Hydroxy-compound	Melting point of ester	Yield (%)	Reaction conditions	
			Temperature	Time (hours)
Methyl alcohol (5 ml)	86.5°	51	In boiling alcohol	15
Ethyl alcohol (5 ml)	85.5	62		15
n-Octadecyl alcohol (3 g)	65.5*	23	110—120°	15
Benzyl alcohol (3 ml)	150	86		6
β-phenylethyl alcohol (2 g)	88.5	39		12
γ-phenylpropyl alcohol (2.5 g)	86.5**	28		15
Phenol (1.5 g)	72	93		5

* Found %: N 6.69, 6.52. $C_{34}H_{40}O_5N_2$. Calculated %: N 6.42.

** Found %: N 9.22, 9.17. $C_{15}H_{14}O_5N_2$. Calculated %: N 9.26.

TABLE 2

Interaction of 2,4-Dinitrochlorobenzene with Ammonium Fluoride in Alcohol

Alcohol	Yield of 2,4-dinitroaniline (%)	Reaction conditions	
		Temperature	Time (hours)
Ethyl	4	In boiling alcohol	10
Benzyl	23	110-120°	5

TABLE 3

Interaction of 2,4-Dinitrobromobenzene (2.47 g, 0.01 mole) with Hydroxy-Compounds in the Presence of Potassium Fluoride (1.16 g, 0.02 mole)

Hydroxy-compound	Melting point of ester	Yield (%)	Reaction conditions	
			Temperature	Time (hours)
Ethyl alcohol (5 ml)	85°	51	In boiling alcohol	15
Benzyl alcohol (3 ml)	150	68	110-120°	6
Phenol (1.5 g)	71.5	74		5

Interaction of 2,4-dinitrochlorobenzene with a toluene solution of benzyl alcohol, in the presence of potassium fluoride. A mixture of 2.03 g of 2,4-dinitrochlorobenzene, 1.16 g of potassium fluoride and 3 ml of benzyl alcohol was heated for six hours in 5 ml of boiling toluene. From the reaction mixture there was obtained 0.17 g (6%) of the benzyl ester of 2,4-dinitrophenol, m. p. 147-149° and 1.76 g (87%) of unchanged 2,4-dinitrochlorobenzene.

Interaction of 2,4-dinitrochlorobenzene with ammonium fluoride in alcoholic solution. 2.03 g of 2,4-dinitrochlorobenzene was heated with 4 times its weight of ammonium fluoride in 5 ml of alcohol. At the end of the reaction the reaction mass was treated with hot dry benzene and the inorganic substances were separated by filtration. The benzene was removed and 2,4-dinitroaniline, m. p. 174-176°, was obtained on recrystallization from alcohol. Mixture of the substance with an authentic sample of 2,4-dinitroaniline (m. p. 178-179°) did not depress the melting point.

Interaction of 2,4-dinitrobromobenzene with potassium fluoride. 2.47 g of 2,4-dinitrobromobenzene was heated with 0.7 g of potassium fluoride for seven hours at 180-200°. Yield of 2,4-dinitro fluorobenzene as determined by titration of the bromide ion formed, 63%.

Interaction of 2,4-dinitrobromobenzene with hydroxy-compounds in the presence of potassium fluoride. The reactions were carried out under the same conditions as the corresponding reactions with 2,4-dinitrochlorobenzene. The proportions of reagents and the reaction conditions are given in Table 3.

SUMMARY

1. By heating 2,4-dinitrochlorobenzene with anhydrous potassium fluoride at 190-200° the authors have prepared 2,4-dinitrofluorobenzene in a yield of over 90%.

2. By interacting 2,4-dinitrochlorobenzene with ammonium fluoride, 2,4-dinitroaniline was obtained in a yield of over 70%.

3. By heating 2,4-dinitrochlorobenzene with potassium fluoride in various hydroxy compounds the corresponding esters of 2,4-dinitrophenol were obtained.

4. 2,4-Dinitrobromobenzene reacts in a manner similar to the chloro-derivative, but at a slower rate.

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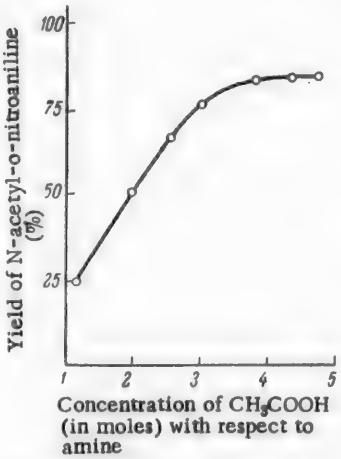
ON THE INTERACTION OF KETENE WITH NITROGENOUS BASES

III. ACETYLATION OF PRIMARY AROMATIC AMINES WITH KETENE

Yu. V. Svetkin

The acetylating properties of ketene have been first described by Wilsmore and Sterwart [1]. Up to the present acetylation of primary aromatic amines with ketene has been confirmed in the case of aniline, o- and p-toluidines [2], o- and p-aminophenols, hydrazines, nitroanilines and methylanilines. The literature records no other data on this reaction. On the other hand, it has been shown by Van-Alphen [3] that o- and p-nitroanilines, tribromoaniline, picramide, phenylhydrazine hydrochloride and diphenylamine do not react with ketene under normal conditions in the absence of catalysts. From what has been said above it will be appreciated that the interaction of ketene with aromatic amines has not been investigated sufficiently and that, in addition, there are many contradictions as regards the results. Thus, Schmidlin and Bergmann [4], on the basis of the reaction between ketene and aniline, have stated that ketene is a vigorous acetylating agent, while Van-Alphen [3] came to the conclusion that it is a weak acetylating agent. Rice and co-workers [5] have again upheld the viewpoint of Schmidlin and Bergmann. Later, Hurd and Roe [6] confirmed the long-known and repeatedly confirmed fact that phenols can be acetylated with ketene only in the presence of catalysts. In 1952, N. V. Smirnov, A. P. Skoldinov and K. A. Kocheshkov [7] have shown that ketene reacts with acid amides in the presence of catalytic amounts of phosphoric acid, sulfuric acid, benzenesulfonic acid, etc. There are also other communications on the chemistry of ketene which command attention.



Acetylating of o-nitroaniline.

It is well-known that acetic anhydride and acetyl chloride react relatively easily with amines and acid amides while ketene itself does not interact with these compounds in the absence of catalysts [8-10]. All this evidence makes one proceed with caution when examining the acetylating properties of ketene. In this connection it must be pointed out that the weakest link in existing theories of the reactivity of ketene is the single-step mechanism in the interaction of ketene with amines:

$$CH_2=C=O + R-NH_2 \rightarrow CH_3CO-NH-R$$

Such a picture of the reaction is at variance with experimental facts since it is well-known that catalytic reactions do not take place by a single-step interaction between the reagents, but proceed according to a more complex mechanism. In the present work the acetylation of very diverse primary aromatic amines with ketene has been studied. We were able to confirm that dry amines do not react with ketene in anhydrous solvents. Another very interesting fact is that in the presence of water some amines undergo acetylation by ketene through an intermediate stage involving the formation of acetates. It is also certain that the reaction passes through this stage in the presence of acetic acid. In the case of nitroanilines it is found that the ortho isomer can be acetylated with ketene only in the presence of acetic acid and that the rate of reaction depends on the concentration of the acip up to a certain limiting concentration

Expt. No.	Original amine	Solvent (ml)	Consumption of acetone for pyrolysis (ml)	Maximum reaction temp.	Ratio of amine to catalyst (moles)	M.p. of acetyl derivative	Yield (%)	Remarks
1	m-Nitroaniline	Toluene (30)	65	28°	1 : 0.1 CH_3COOH	152°	82	Similar results were obtained in ether and benzene as solvents
2	The same	The same	65	28	1 : 0.1 H_2O	152	82	
3	p-Nitroaniline	The same	30	40	1 : 3 CH_3COOH	213	93	
4	Naphthylamine	(50)	60	22	1 : 0.01 H_2O	159	86	The reaction proceeds through a stage involving the formation of the corresponding acetates [11]
5	The same	The same	60	30	1 : 0.01 CH_3COOH	159	92	
6	p-Naphthylamine	"	60	22	1 : 1 H_2O	134	86	
7	The same	"	60	30	1 : 0.01 CH_3COOH	134	86	
8	Cyclohexylamine	Acetone (30)	20	20	1 : 1 H_2O	104	92	
9	The same	The same	20	20	1 : 0.1 CH_3COOH	104	92	
10	Cyclohexylamine + + acetic acid	"	20	20	1 : 1 CH_3COOH	104	92	
11	Cyclohexylamine + propionic acid	"	20	20	1 : 1 C_2H_5COOH	104	92	
12	p-Chloroaniline	Toluene (40)	40	32	1 : 0.1 CH_3COOH	177	81	
13	The same	The same	40	32	1 : 0.1 H_2O	177	81	
14	p-Bromaniline	"	—	25	1 : 0.01 CH_3COOH	168	87	
15	p-Iodaniline	Toluene (40)	40	42	1 : 0.1 CH_3COOH	181—182	83	
16	The same	The same	40	42	1 : 0.1 H_2O	181—182	83	
17	p-Nitrosoaniline	"	40	30	1 : 0.1 CH_3COOH	175	81	
18	p-Phenetidine	"	70	23	1 : 0.1 H_2O	136—138	86	
19	o-Aminophenol	Alcohol (60)+ ether 3	200	35	1 : 3 CH_3COOH	205	72	
20	o-Anisidine	(30)	70	40	1 : 1 H_2O	78	82	
21	The same	The same	70	40	1 : 0.1 CH_3COOH	78	82	
22	p-Anisidine	Toluene (60)	70	48	1 : 0.1 CH_3COOH	132	80	On dissolution of N-acetyl-p-anizidine in Conc. HNO_3 at 10° there formed 2,3-dinitroacetaminoanisole, m.p. 230-232°
23	The same	The same	70	30	1 : 1 H_2O	132	80	

(continued)

Expt. No.	Original amine	Solvent (ml)	Consumption of acetone for pyrolysis (ml)	Maximum reaction temp.	Ratio of amine to catalyst (moles)	M.p. of acetyl derivative	Yield (%)	Remarks
24	p-Aminophenol	Alcohol (60)	200	50	1 : 3 CH_3COOH	167–168	74	
25	p-Chloro-o-aminophenol	Alcohol (40)	30	42	1 : 0.01 CH_3COOH	175–176	80	Found %: Cl 18.80, 18.87. Calculated %: Cl 19.10
26	The same	The same	30	42	1 : 0.1 H_2O	175–176	80	Found %: CH_3CO 22.9. Calculated %: CH_3CO 23.16
27	p-Nitro-o-aminophenol	The same	30	45	1 : 0.01 CH_3COOH	257–258	88	
28	The same	The same	30	45	1 : 0.1 H_2O	257–258	88	Found %: CH_3CO 20.86. Calculated %: CH_3CO 21.93

Note: On saponification of the acetyl derivatives (Expt. Nos. 1-28) the original amines were obtained.

beyond which neither the reaction time can be shortened nor the yield of the product increased (see figure). A similar relationship is found in the case of p-nitroaniline except that in this case the time necessary for acetylation is shortened by about 4-5 times. It appears that m-nitroaniline reacts with ketene very rapidly since acetylation is complete within 3-4 minutes. Acetylation with ketene proceeds with the greatest difficulty in the case of aminophenols which fact may be explained as being due to the presence in these compounds of strong hydrogen bonds. As regards other amines investigated it may be said that no essential differences in their behavior during acetylation have been observed.

EXPERIMENTAL

Acetylation of aromatic amines with ketene in the presence of water or acetic acid. General method. Into a 4-necked flask provided with a mechanical stirrer was placed 2 g of the amine dissolved in 60 ml of the solvent. To this solution was added a small amount of water or of acetic acid. The contents of the flask were stirred for 10 minutes and ketene was passed during 0.5-1.5 hours (the rate of flow of acetone into the pyrolyzer was 200 ml/hr). After a time the temperature usually reached a maximum and thereafter began to drop; this was taken as an indication that the reaction was complete. The supply of ketene was then interrupted and the mixture was stirred for another 10-20 minutes. The solvent was partly removed and the residue was transferred into a porcelain dish where the products of reaction crystallized. In some cases the acetyl derivatives were obtained in the form of a crystalline precipitate immediately at the end of the reaction. In such cases the precipitates were simply separated by filtration and were washed. The purity of the products was determined from the percentage of the acetyl group by the usual method. In the absence of water or acetic acid in solutions in ether, acetone, carbon tetrachloride, benzene and toluene no acetylation of the amines by ketene could be observed. The results of the acetylation reactions are summarized in the table; the acetylation of o-nitroaniline is presented in the form of a graph.

SUMMARY

1. Primary aromatic amines easily undergo acetylation by ketene in the presence of water or of acetic acid and the reaction proceeds through a stage in which the corresponding acetates are formed.

2. o-p-Aminophenols, o-p-nitroanilines can be acetylated with ketene only with difficulty; this appears to be due to the presence in these compounds of strong hydrogen bonds.

3. Acetylation of o-nitroaniline has been accomplished under normal conditions. The yields of the acetyl derivative was considerably higher than the yields obtained by existing methods.

4. N-acetyl-4-nitro-2-aminophenol which has so far not been described in the literature, has been prepared.

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ON THE INTERACTION OF EPICHLOROHYDRIN AND THE METHYL ETHER OF GLYCIDOL WITH ORGANOCHLOROSILANES

M. S. Malinovsky and M. K. Romantsevich

A considerable number of papers have been devoted to the study of the interaction of epichlorohydrin with various acidic, alkaline and neutral reagents. These investigations show that the α-oxide ring of epichlorohydrin opens up in the direction of the carbon atom with the least number of hydrogen atoms, irrespective of the nature of the reagents [1]. This rule has also been confirmed in the case of the interaction of epichlorohydrin with halogen compounds of arsenic and antimony (arsenic trichloride [2], antimony trichloride [3]). The methyl ether of glycidol also reacts in a manner similar to that observed in the case of epichlorohydrin; in this case the hydroxyl group which is formed is also linked to the secondary carbon atom. This type of addition to epichlorohydrin and to the methyl ether of glycidol appears to be due to the so-called vicinal effect [4].

The interaction of α-oxides with organochlorosilanes has so far not been investigated sufficiently. The few existing papers dealing with the subject are mainly concerned with reactions of organochlorosilanes with ethylene oxide [5]. Recently there appeared a paper by K. A. Andrianov and co-workers [6] in which the authors reported their findings on the interaction of epichlorohydrin and glycidol with organochlorosilanes. According to these authors, these α-oxide compounds react with compounds of the type R_nSiCl_{4-n} according to the following equations

$$R_nSiCl_{4-n} + (4-n)H_2C\underset{\diagdown\,O\,\diagup}{-}CHCH_2Cl \rightarrow R_nSi(OCH_2CHClCH_2Cl)_{4-n} \quad (1)$$

$$R_nSiCl_{4-n} + (4-n)H_2C\underset{\diagdown\,O\,\diagup}{-}CHCH_2OH \rightarrow R_nSi(OCH_2CHClCH_2OH)_{4-n} \quad (2)$$

Equation (1) has been confirmed by the above authors by the presence of glyceryl α,β- or α, γ-dichlorohydrin in the products of hydrolysis of one of the ethers obtained. Confirmation of the structure of the dichlorohydrin in question was conducted by the authors on the supposition that α, β-dichlorohydrin would not yield epichlorohydrin on treatment with alkalis whereas the latter is, in fact, normally prepared from α, γ-dichlorohydrin by this method. Since on treating the products of hydrolysis with potassium hydroxide no epichlorohydrin was detected the authors concluded that it was glyceryl α,β-dichlorohydrin which was present in the hydrolyzate.

However, when reviewing the literature dealing with this problem we found indications of the possibility of actually obtaining epichlorohydrin from glyceryl α,β-dichlorohydrin by treatment with alkali [7]. Kinetic investigations [8, 9] show that the velocity constant of alkaline saponification of α, β-dichlorohydrin to epichlorohydrin is approximately 150 times smaller than in the case of the α,γ-dichlorohydrin. The velocity constant of saponification of the latter is so much greater that even at a temperature of 18-20° it is completely transformed into epichlorohydrin within 3 minutes.

The results obtained by Andrianov and co-workers [6] are also at variance with data found in the literature with regard to the opening of the oxide ring in epichlorohydrin and also with our own experimental data which have been published prior to the appearance of the above paper.

In the present work we have investigated the interaction of epichlorohydrin with the following organochlorosilanes: CH_3SiCl_3, $(CH_3)_2SiCl_2$, $(CH_3)_3SiCl$, ClH_2SiCl_2, $C_2H_5SiCl_3$, $(C_2H_5)_2SiCl_2$, $(C_2H_5)_3SiCl$ and $C_2H_5SiHCl_2$, and we have established that the reaction proceeds according to the following scheme:

$$R_nSiCl_{4-n} + (4-n)H_2C(O)CHCH_2Cl \rightarrow R_nSi\left(OCH\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix}\right)_{4-n} \quad (3)$$

i. e., the oxide ring of epichlorohydrin opens in the direction of the carbon atom with the least number of hydrogen atoms. The structure of the compounds obtained (and hence, also, the mechanism (3))was confirmed by hydrolysis and oxidation of the products of hydrolysis with chromic acid. In all cases there was obtained, in good yield, symmetrical dichloroacetone whose constants as well as the melting point of the semicarbazone correspond to literature data. The formation of symmetrical dichloroacetone proves beyond doubt the structure of the compounds indicated above (Eq. (3)), prepared from epichlorohydrin and organochlorosilanes and therefore confirms the rule governing the opening of the oxide ring in epichlorohydrin.

There are certain other inaccuracies in the paper of Andrianov and co-workers which must be pointed out. There is considerable discrepancy between the determined and calculated values of MR (Table 1 in the paper in question): for example, a value of 64.80 was found for dimethyl-2,3-chlorodipropoxysilane whereas the calculated value is 69.70 (a difference of 4.9); similarly the measured and calculated values of MR for trimethyl-2,3,-chloropropoxysilane were, respectively, 45.4 and 49.0 (a difference of 3.6), and so on. These results would indicate that the authors were working with impure compounds. Finally, there is some doubt as to the synthesis of triethyl-2,3-chloropropoxysilane (from epichlorohydrin and triethylchlorosilane). The condensation was carried out by heating the reaction mixture at 40-50° for 10 hours. After distillation in vacuo there was obtained triethyl-2,3-chloropropoxysilane (15.8 g), boiling at 65-70° at 100 mm pressure. When attempting to repeat the reaction under the conditions described by these authors we have failed to achieve condensation. At the temperature reported as the boiling point of the ether described by the authors the unchanged reagents were found to come over. It also strikes the eye that the boiling point of this ether (65-70° at 100 mm) is too low by comparison with a boiling point of 96-100° at 66 mm for the lowest-boiling ether obtained from epichlorohydrin and trimethylchlorosilane. It is obvious that the physical constants and the analytical results reported by the authors refer not to a single compound but to a mixture of the reagents for which we have found the same constants as those given by Andrianov. Even after heating the reagents on the water bath for 80 hours there was no sign of any condensation.

We have also condensed the methyl ether of glycidol with the alkylchlorosilanes enumerated above (with the exception of triethylchlorosilane). The structures of the resultant compounds were established by hydrolysis followed by oxidation of the hydrolyzate. Since no constants could be found in the literature for the expected α-methoxy-γ-chloroacetone which would be formed on oxidation in the event of the oxide ring opening towards the secondary carbon atom, we reduced the chloroketone with zinc dust in acetic acid to the known methoxyacetone:

$$ClCH_2—CO—CH_2—OCH_3 \xrightarrow{H_2} CH_3—CO—CH_2—OCH_3 + HCl$$

This ketone was, in fact, obtained, thus confirming beyond doubt that the oxide ring in the methyl ether of glycidol opens up according to scheme (4):

$$R_nSiCl_{4-n} + (4-n)H_2C(O)CHCH_2OCH_3 \rightarrow R_nSi\left(OCH\begin{matrix}CH_2Cl\\CH_2OCH_3\end{matrix}\right)_{4-n} \quad (4)$$

The condensation of epichlorohydrin and of the methyl ether of glycidol with alkylchlorosilanes does, of course, take place in two steps. In the first step there is formed, from the α-oxide and hydrogen chloride (traces of which are found in alkylchlorosilanes), the corresponding halogenhydrin; for example, in the case of epichlorohydrin:

$$H_2C(O)CHCH_2Cl + HCl \rightarrow ClCH_2CH(OH)CH_2Cl \quad (5)$$

TABLE 1

Compounds Obtained by Condensation of Epichlorohydrin with Organochlorosilanes

No.	Formula	Yield (%)	Boiling point (pressure in mm Hg)	n_D^{20}	d_4^{20}	MR_D		Analysis (%)			
								Cl		Si	
						found	calcd.	found	calcd.	found	calcd.
1	$(CH_3)_2SiOCH(CH_2Cl)_2$	62.2	105—107° (68)	1.4394	1.0762	49.57	49.98	35.02, 35.40	35.25	13.88, 14.04	13.95
2	$(CH_3)_2Si(OCH(CH_2Cl)_2)_2$	76.2	135—137 (3)	1.4771	1.2791	69.40	69.68	45.29, 45.18	45.15	8.87, 8.94	8.94
3	$CH_3Si(OCH(CH_2Cl)_2)_3$	77.3	202—204 (3)	1.4912	1.3894	89.05	89.38	49.72, 49.93	49.81	6.43, 6.48	6.58
4	$(CH_3)HSi(OCH(CH_2Cl)_2)_2$	87.5	132 (3.5)	1.4802	1.3124	64.98	65.31	47.29, 47.21	47.27	9.30, 9.26	9.36
5	$(C_2H_5)_2Si(OCH(CH_2Cl)_2)_2$	73.5	136—138 (2)	1.4786	1.2352	78.49	78.94	41.22, 41.44	41.45	8.09, 8.15	8.21
6	$C_2H_5Si(OCH(CH_2Cl)_2)_3$	77.5	191—193 (2)	1.4915	1.3634	93.79	94.01	48.21, 48.19	48.23	6.19, 6.29	6.37
7	$(C_2H_5)HSi(OCH(CH_2Cl)_2)_2$	—	139 (3.5)	1.4799	1.2805	69.67	69.64	45.19, 44.95	45.15	8.87, 8.83	8.94

TABLE 2

Compounds Obtained by Condensation of the Methyl Ether of Glycidol with Organochlorosilanes

No.	Formula	Yield (%)	Boiling point (pressure in mm Hg)	n_D^{20}	d_4^{20}	MR_D		Analysis (%)			
								Cl		Si	
						found	calcd.	found	calcd.	found	calcd.
1	$CH_3Si\left(OCH\begin{matrix}CH_2OCH_3\\CH_2Cl\end{matrix}\right)_3$	29.3	170—170.5° (3)	1.4579	1.2054	93.65	94.06	25.78, 25.55	25.72	6.88, 6.65	6.79
2	$(CH_3)_2Si\left(OCH\begin{matrix}CH_2OCH_3\\CH_2Cl\end{matrix}\right)_2$	71.4	119.5—120 (5)	1.4495	1.1321	72.39	72.80	23.24, 23.47	23.23	9.30, 9.15	9.20
3	$(CH_3)_3SiOCH\begin{matrix}CH_2OCH_3\\CH_2Cl\end{matrix}$	77.1	86.5—88 (30)	1.4273	0.9956	50.79	51.54	18.09, 17.90	18.02	14.18, 14.32	14.28
4	$(CH_3)HSi\left(OCH\begin{matrix}CH_2OCH_3\\CH_2Cl\end{matrix}\right)_2$	76	118.5—120 (5)	1.4495	1.1491	68.04	68.43	24.19, 24.32	24.35	9.74, 9.59	9.64
5	$C_2H_5Si\left(OCH\begin{matrix}CH_2OCH_3\\CH_2Cl\end{matrix}\right)_3$	72.2	181—183 (4)	1.4599	1.1968	97.89	98.69	24.88, 25.02	24.86	6.67, 6.52	6.57
6	$(C_2H_5)_2Si\left(OCH\begin{matrix}CH_2OCH_3\\CH_2Cl\end{matrix}\right)_2$	66.4	137—138 (4)	1.4588	1.1202	81.30	86.06	21.28, 21.17	21.27	8.36, 8.50	8.43
7	$(C_2H_5)HSi\left(OCH\begin{matrix}CH_2OCH_3\\CH_2Cl\end{matrix}\right)_2$	72.5	128—130 (4)	1.4513	1.1396	72.17	73.06	23.10, 33.41	23.23	9.32, 9.25	9.20

The second step involves alcoholysis of the organochlorosilane by the chlorohydrin formed, with regeneration of hydrogen chloride:

$$_nSiCl_{4-n} + (4-n)HOCH\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix} \rightarrow R_nSi\left(OCH\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix}\right)_{4-n} + (4-n)HCl \quad (6)$$

EXPERIMENTAL

1. Tri-(α,γ-dichloroisopropoxy)-methylsilane. Into a 3-necked flask provided with a mechanical stirrer, reflux condenser, dropping funnel and thermometer, was placed 14.95 g of methyltrichlorosilane. From the dropping funnel 29.76 g of epichlorohydrin was added at a rate such that the temperature of the reaction mixture did not exceed 30-35°. The reaction mixture was then heated at 50-60° for 10 hours and allowed to stand overnight. The reaction product was fractionated in vacuo. Tri-(α,γ-dichloroisopropoxy)-methylsilane was collected at 202-204.5° (at 3 mm), yield 33 g (77.3%). The constants of the compound are given in Table 1.

All other condensations with epichlorohydrin were effected in a manner similar to that described above.

2. Hydrolysis and oxidation of tri-(α,γ-dichloroisopropoxy)-methylsilane. Into a 3-necked flask provided with a mechanical stirrer, reflux condenser, dropping funnel and thermometer, was placed 12.5 g of sodium dichromate, 10 ml of water and 14 g of the above silane ether. A solution of 15 g of concentrated sulfuric acid in 5 ml of water was added slowly from the dropping funnel over six hours, the rate of addition being such that the temperature of the reaction mixture did not exceed 20-25°. After addition of all the acid the reaction mixture was stirred at room temperature for another five hours. The oxidation product was extracted with diethyl ether and after removal of the latter the residue was distilled at normal pressure. 5 g of the fraction boiling at 170-175° was collected; m. p. 44-45°; the semicarbazone melts at 119-120° (from alcohol). The constants of the substance and the melting point of the semicarbazone are in agreement with literature data for α,γ-dichloroacetone [10]. The substance also forms a bisulfite. The structure of the other ethers synthesized was confirmed in the same manner.

3. Interaction of epichlorohydrin with triethylchlorosilane. 6.5 g of epichlorohydrin and 10 g of triethylchlorosilane were reacted under conditions described above. 16 g of the substance was fractionated and the following fractions were collected (at 100 mm): fraction 1, b. p. 42-60°, 0.9 g; fraction 2, 60-65°, 1.5 g; fraction 3 65-70°, 6.6 g; fraction 4, 70-90°, 2.1 g. The residue in the flask weighed 4.3 g. On shaking with aqueous silver nitrate solution all the fractions gave a copious precipitate of silver chloride which indicates labile chlorine, i. e., the presence of unreacted triethylchlorosilane. Fraction 3 had the constants reported by Andrianov and co-workers, [6], i. e., n_D^{20} 1.4492 and d_4^{20} 1.0776. At normal pressure it distilled between 115 and 1[illegible]° (epichlorohydrin boils at 117° and triethylchlorosilane at 143°). The residue in the flask also gave the reaction for labile chlorine which shows that it does not contain any of the condensation product.

4. Condensation of methyl ether of glycidol with methyltrichlorosilane. 27.43 g of the methyl ether of glycidol and 14.95 g of methyltrichlorosilane were condensed by the method described above but with the difference that after heating at 60-80° the reaction mixture was heated on a boiling bath for another 5 hours and was then allowed to stand overnight.

42 g of the substance was distilled at 3 mm pressure and the following fractions were collected: fraction 1, 136-170°, 8.7 g; fraction 2, 170-170.5°, 21.4 g; fraction 3, 170.5-195°, 8 g; the residue in the flask weighed 2.6 g. Fraction 1 gave a positive reaction for ionizable chlorine with silver nitrate, indicating the presence of unreacted methyltrichlorosilane. Fraction 2 gave no precipitate of silver chloride with $AgNO_3$. Analysis of this fraction gave results corresponding to formula 1 in Table 2. The properties of the other ethers obtained by condensation of organochlorosilanes with the methyl ether of glycidol are listed in Table 2.

The structures of the ethers were confirmed by oxidation by the method described above, followed by a reduction of α-methoxy-γ-chloroacetone with zinc in acetic acid. In all cases there was obtained methoxyacetone ($CH_3-CO-CH_2-OCH_3$); b. p. 117° at 753 mm, d_4^{20} 0.9558, which is in agreement with literature data [11].

SUMMARY

1. It has been established that in condensations of organochlorosilanes with epichlorohydrin the oxide ring opens in such a manner that the oxygen atom remains attached to the secondary carbon atom.

2. Seven α,γ-dichloroisopropoxyorganosilanes have been prepared and characterized; these compounds have been mistakenly identified in the literature as α,β-dichloropropoxyorganosilanes.

3. The addition of organochlorosilanes to the methyl ether of glycidol has been investigated for the first time. It has been found that the oxide ring opens, as it does also in the case of epichlorohydrin, towards the secondary carbon atom.

4. By condensation of the methyl ether of glycidol with some organochlorosilanes the authors have prepared seven α-methoxy-γ-chloroisopropoxyorganochlorosilanes which have not so far been described in the literature.

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THE USE OF A HEAVY ISOTOPE OF OXYGEN TO STUDY THE MECHANISM OF ALKALI TRANSESTERIFICATION OF ESTERS

R. V. Kudryavtsev and D. N. Kursanov

When esters are reacted with alcohols in the presence of alcoholates, the following equilibrium is established

$$R{-}C(=O){-}O{-}R' + R''OH \underset{}{\overset{R''ONa}{\rightleftharpoons}} R{-}C(=O){-}O{-}R'' + R'OH$$

The position of the equilibrium in this reaction is basically determined by the concentration ratio of the materials entering into the reaction. A shift of the equilibrium to the right can be obtained either by increasing the concentration of one of the starting materials or by decreasing the concentration of one of the end products. In particular, if the ester or alcohol formed has a lower boiling point than the starting ester or alcohol, then by distilling off one of the reaction products as it is formed the equilibrium can be shifted to the right and the reaction brought to completion. Under these circumstances the reaction of alkali transesterification acquires preparative significance.

The present work is devoted to the investigation of the mechanism of this reaction. We carried out the transesterification of the ethyl ester of propionic acid with n-butyl alcohol in the presence of a small amount of sodium butylate.

$$C_2H_5{-}C(=O){-}O{-}C_2H_5 + n\text{-}C_4H_9OH \xrightarrow{C_4H_9ONa} C_2H_5{-}C(=O){-}O{-}C_4H_9 + C_2H_5OH$$

The ethyl propionate was labeled with a heavy isotope of oxygen – in the ester position there was 0.71 at.% of O^{18}, while in the carbonyl oxygen position the concentration of O^{18} was normal (i.e., 0.2% O^{18}). The ethyl alcohol formed in the reaction process was continuously distilled off on a column with an efficiency of 20 theoretical plates. This alcohol was redistilled and analyzed for O^{18} content. It appeared that it contained the whole excess of O^{18} from the starting ester, i.e., 0.71%. It further appeared that the butyl propionate obtained from the reaction contained no excess of O^{18} at all in comparison with its natural concentration.

These data permit us to propose the following reaction scheme

$$C_4H_9O^{\ominus} + C(=O)(C_2H_5){-}O^{18}{-}C_2H_5 \longrightarrow \left[C_4H_9O\cdots C(=O)(C_2H_5)\cdots O^{18}C_2H_5\right]^{\ominus} \longrightarrow C_4H_9OC(=O)C_2H_5 + {}^{\ominus}O^{18}C_2H_5$$

$$C_2H_5O^{\ominus 18} + C_4H_9OH \longrightarrow C_2H_5O^{18}H + C_4H_9O^{\ominus}$$

A small amount of the alcoholate was necessary to start the reaction and was not spent in the reaction process.

Thus the alkali transesterification of esters is a reaction of nucleophilic substitution on the carbonyl carbon and like the alkali hydrolysis of such esters it proceeds with the rupture of the acyl–oxygen bond.

EXPERIMENTAL

Ethyl propionate – O^{18}. To 26 g of anhydrous ethyl alcohol containing 0.71% O^{18} (for method of preparing heavy-oxygen ethyl alcohol see [1]) and 45.5 g of anhydrous pyridine was added from a dropping funnel, while stirring vigorously, 52.6 g of propionyl chloride. The reaction was completed in 2-2.5 hours. The mixture was treated with water, the ester layer was separated, dried with magnesium sulfate, and the ethyl propionate was distilled at 98° (732 mm); n_D^{20} 1.3840, d_4^{20} 0.8902.

Alcoholysis of labeled ethyl propionate with n-butyl alcohol. 0.2 g of metallic sodium was dissolved in 25 ml (20.3 g) of n-butyl alcohol (b.p. 116.5-117° at 740 mm, n_D^{20} 1.3993, d_4^{20} 0.8098) and 6 ml (5.3 g) of labeled ethyl propionate was added. The reaction was carried out in a vessel with a column having an efficiency of 20 theoretical plates, with continuous removal by distillation of the ethyl alcohol formed. The alcohol was then redistilled over calcium hydride, b.p. 78°. n_D^{20} 1.3642, d_4^{20} 0.7898, and was analyzed for O^{18} content. Results of analysis: 0.71 and 0.65%. The mixture remaining in the distilling flask after distilling off the ethyl alcohol consisted of butyl propionate, butyl alcohol, and sodium butylate. After distilling off most of the butyl alcohol, we poured the contents of the flask into 200 ml of water; the remaining butyl alcohol then went into the water layer, and the alcoholate was decomposed. The ester layer was separated and washed several times with water. The ester was diluted with benzene. After the benzene was distilled off, the butyl-propionate was distilled: b.p. 145°, n_D^{20} 1.4014, d_4^{20} 0.8741. Results of isotopic analysis of oxygen: 0.20 and 0.20% O^{18}.* All of the isotopic analyses were carried out by the method worked out by I. P. Gragerov in the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR [2].

SUMMARY

The mechanism of alkali transesterification of esters has been investigated with the aid of a heavy isotope of oxygen in the instance of the reaction of labeled ethyl propionate with normal primary butyl alcohol in the presence of sodium butylate. It has been shown that this reaction, like the alkali hydrolysis of esters of similar structure, proceeds with the rupture of the acyl-oxygen bond in the ester.

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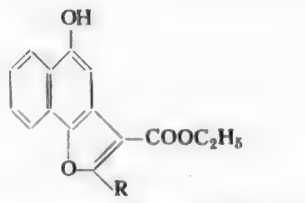
INVESTIGATIONS IN THE FIELD OF QUINONES

XVIII. SYNTHESIS OF SUBSTITUTED NAPHTHOFURANS

A. N. Grinev, G. K. Prokofyeva and A. P. Terentyev

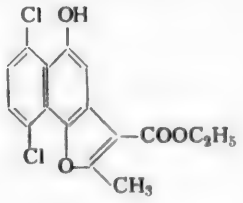
The condensation of p-quinones with acetoacetic ester and its analogs, has been shown in our previous publications [1, 2], proceeds with the initial formation of a carbon-carbon bond and leads to the synthesis of 5-hydroxy-substituted benzofurans. In one of our investigations it was established that α-naphthoquinone also enters into reaction with acetoacetic and benzoacetic esters, with the production of high yields of derivatives of the naphthofuran series [3].

Now we have succeeded in carrying out the condensation of α-naphthoquinone with the near homologs and some analogs of acetoacetic ester. By the action on α-naphthoquinone of butyroacetic, isobutyroacetic, and p-nitrobenzoacetic esters a series of naphthoquinones was obtained (I), (II), (III).



R = $CH_2CH_2CH_3$, $CH(CH_3)_2$, $C_6H_4NO_2$

(I) (II) (III)



IV

The condensation of 5,8-dichloro-1,4-naphthoquinone, obtained by the oxidation of 1,4-dichloronaphthalene [7], with acetoacetic ester produced the dichloro-substituted naphthofuran (IV).

EXPERIMENTAL

2-Propyl-3-carboethoxy-5-hydroxynaphthofuran (I). In a three-necked flask fitted with a mechanical stirrer and a reflux condenser were placed 6.32 g of zinc chloride, 6 ml of anhydrous alcohol, and 13 g of butyroacetic ester. The mixture was heated at 100° until the zinc chloride completely dissolved. To the solution that was formed was added 7.25 g of α-naphthoquinone and the mixture was heated for 40 minutes on a boiling water bath. The crystals that formed were separated and recrystallized. Yield 10 g (77%). M.p. 164° (from alcohol).

Found %: C 72.19, 72.16; H 5.98, 5.99. $C_{18}H_{18}O_4$. Calculated %: C 72.46; H 6.08.

2-Propyl-3-carboxy-5-hydroxynaphthofuran (V) was obtained by saponification of ester (I) with alcoholic alkali. For the experiment 5 g of (I), 4.63 g of sodium hydroxide, and 70 ml of alcohol were taken. The acid (V) was recrystallized from 50% acetic acid. Yield 4.35 g (quantitative). M.p. 240° (in a sealed capillary).

Found %: C 70.98, 70.85; H 5.33, 5.41. $C_{16}H_{14}O_4$. Calculated %: C 71.11; H 5.15.

2-Propyl-3-carboethoxy-5-benzoxynaphthofuran (VI). To a solution of 1 g of the naphthofuran derivative (I) in 3 ml of pyridine was added 0.5 g of benzoyl chloride while cooling with ice and stirring. The reaction solution was left at room temperature for 4 hours, then diluted with water. The crystals that formed were washed with 10% sulfuric acid and water. 1.2 g of crystals were obtained. M.p. 110-112° (from a mixture of alcohol and dioxane 10 : 1).

Found %: C 74.21, 74.46; H 5.40, 5.42. $C_{25}H_{22}O_5$. Calculated %: C 74.61; H 5.51.

2-Isopropyl-3-carboethoxy-5-hydroxynaphthofuran (II). The condensation was carried out under the conditions used to prepare the naphthofuran (I). For the experiment 3.2 g of α-naphthquinone, 5 g of isobutyroacetic ester, 2.8 g of zinc chloride, and 3.5 ml of anhydrous alcohol were taken. The crystals were separated and recrystallized. Yield 3.3 g. M. p. 151-152° (from ligroin).

Found %: C 72.50, 72.35; H 6.34, 6.42. $C_{18}H_{18}O_4$. Calculated %: C 72.46, H 6.08.

2-p-Nitrophenyl-3-carboethoxy-5-hydroxynaphthofuran (III). The reaction was carried out in a manner analogous to the preparation of the naphthofuran (I). For the experiment 7.8 g of α-naphthoquinone, 12 g of p-nitrobenzoacetic ester, 6.8 g of zinc chloride, and 6.5 ml of anhydrous alcohol were taken. The mixture was heated for 30 minutes at 120-130°. Red crystals were filtered off and washed with ether. Yield 14.3 g (76%). M.p. 250-251° (from nitrobenzene).

Found %: C 66.98, 67.00; H 4.28, 4.17. $C_{21}H_{15}O_6N$. Calculated %: C 66.83; H 3.98.

2-Methyl-3-carboethoxy-5-hydroxy-6,9-dichloronaphthofuran (IV). The reaction was carried out under the conditions used for the preparation of (I). For the experiment 3.6 g of 5,8-dichloro-1,4-naphthoquinone, 8 ml of acetoacetic ester, 2.32 g of zinc chloride, and 3 ml of anhydrous alcohol were taken. The crystals obtained from the reaction were separated out, washed with ether, and dried. Yield 4.5 g (85%). M.p. 183° (from alcohol).

Found %: C 56.84, 56.70; H 3.74, 3.79. $C_{16}H_{12}O_4Cl_2$. Calculated %: C 56.63; H 3.54.

2-Methyl-3-carboxy-5-hydroxy-6,9-dichloronaphthofuran (VII) was obtained by saponification of ester (IV) with alcoholic alkali. For the experiment 0.99 g of (IV), 1 g of NaOH, and 15 ml of alcohol were taken. Yield of (VII) 0.96 g (96%). M.p. 330° (with decomp). For analysis the acid was recrystallized from 50% acetic acid.

Found %: C 54.15; H 2.78. $C_{14}H_8O_4Cl_2$. Calculated %: C 54.03; H 2.57.

SUMMARY

By the condensation of 1,4-naphthoquinone and 5,8-dichloro-1,4-naphthoquinone with esters of β-keto-acids a series of substituted naphthofurans has been prepared.

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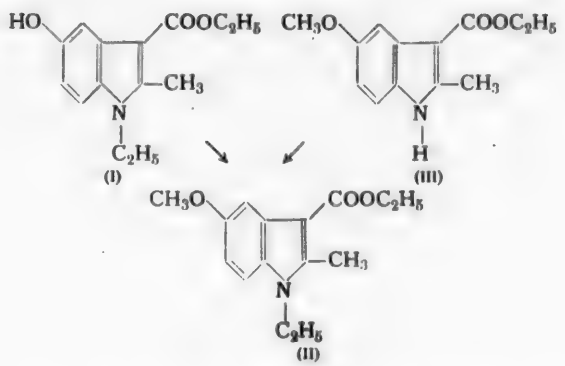
INVESTIGATIONS IN THE FIELD OF QUINONES

XIX. SYNTHESIS OF SOME N-ALKYLSUBSTITUTED INDOLES

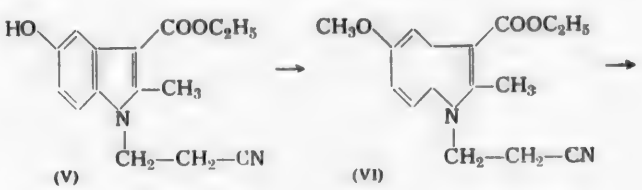
A. N. Grinev, N. E. Rodzevich and A. P. Terentyev

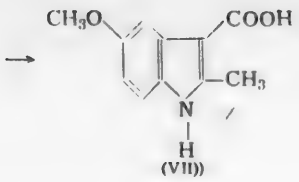
In our previous publications it has been shown that the condensation of quinones with esters of β-aminocrotonic acid and its analogs is a convenient method for the synthesis of derivatives of the indole series [1, 2]. Esters of N-methyl- and N-ethylaminocrotonic acids also enter into reaction with quinones [2, 3].

In the present work a series of substituted indoles has been prepared by the condensation of N-ethyl- and N-cyanoethyl-β-aminocrotonic acids with p-benzoquinone and of the ester of N-ethyl-β-aminocrotonic acid with α-naphthoquinone. We have succeeded in improving the method of carrying out the reaction, permitting a significant increase in the yield of the indoles. 1-Ethyl-2-methyl-3-carboethoxy-5-hydroxyindole (I), synthesized in 75% yield, was converted by methylation into 1-ethyl-2-methyl-3-carboethoxy-5-methoxyindole (II). The latter was also obtained by the alkylation in nitrogen with ethyl bromide of the known [4] 2-methyl-3-carboethoxy-5-methoxyindole (III).



By the condensation of the ethyl ester of N-cyanoethyl-β-aminocrotonic acid (IV), prepared by us, with p-benzoquinone we synthesized 1-cyanoethyl-2-methyl-3-carboethoxy-5-hydroxyindole (V). The structure of this compound was proved by the fact that by heating 1-cyanoethyl-2-methyl-3-carboethoxy-5-methoxyindole (VI), which was obtained from it by the method worked out in our laboratory [5], with a concentrated solution of sodium hydroxide, the known [1, 4] 2-methyl-3-carboxy-5-methoxyindole (VII) was produced.





(VII)

The evidence obtained by us of the structure of the substituted indoles permits us to assume that the condensation of esters of N-alkylaminocrotonic acids with quinones proceeds with the initial formation of a carbon-carbon bond and leads to 5-hydroxysubstituted indoles.

In our work with V. I. Shvedov [1, 2] it was found that the imine of acetylacrtone reacted with p-benzoquinone with the formation of substituted indole and benzofuran, but the reaction of the N-phenylimine of acetylacetone with p-benzoquinone produced only the substituted indole. With the objective of synthesizing N-alkyl-3-acetyl derivatives of indole, we carried out the condensation of the N-methyl- and N-ethylimine of acetylacetone with p-benzoquinone. However, as a result of the reaction carried out under the conditions used for the reaction of acetylacetone imine with p-benzoquinone only 2-methyl-3-acetyl-5-hydroxybenzofuran (VIII) was obtained.

EXPERIMENTAL

1-Ethyl-2-methyl-3-carboethoxy-5-hydroxyindole (I). 10 g of p-benzoquinone was dissolved in 36 ml of dry acetone. To the cooled mixture was added 18 g of the ethyl ester of N-ethyl-β-aminocrotonic acid while cooling with ice and stirring. The reaction solution was left at room temperature, whereupon reaction started and the mixture warmed up to boiling. After the boiling ceased, the dark-red reaction solution was heated for 1.5 hours on a boiling water bath. The resulting solution was left for the night at room temperature for the solvent to evaporate. The crystals that precipitated were worked up. Yield 15 g (75%). M.p. 184.5° (from dioxane).

Found %: 68.26, 68.09; H 7.11, 7.05. $C_{14}H_{17}O_3N$. Calculated %: C 67.99; H 6.93.

1-Ethyl-2-methyl-3-carboethoxy-5-methoxyindole (II). To 7.1 g of 1-ethyl-2-methyl-3-carboethoxy-5-hydroxyindole were added 36 ml of 2 N NaOH and 7 ml of dioxane. To the solution obtained by heating to 35-40° was added 6.6 g of dimethyl sulfate (with shaking and in portions). Mixing of the materials and the reaction were carried out in an atmosphere of nitrogen. In the process of adding the dimethyl sulfate the reaction mixture heated up. To complete the reaction the solution was heated for 40 minutes on a boiling water bath. An oil layer was formed, which started to crystallize upon cooling. The crystals were separated out. The dioxane was distilled off from the mother liquor in vacuo and the crystals that precipitated were filtered off. Yield 8 g (97%). M. p. 67° (from methanol).

Found %: C 68.83, 69.08; H 7.40, 7.59. $C_{15}H_{19}O_3N$. Calculated %: C 68.94; H 7.33.

1-Ethyl-2-methyl-3-carboxy-5-methoxyindole (IX). 2 g of 1-ethyl-2-methyl-3-carboethoxy-5-methoxyindole was boiled in 18 ml of 2 N NaOH for 2.5 hours. The solution was filtered and the filtrate was acidified with acetic acid to an acid reaction. Crystals of acid (IX) were filtered off. Yield 1.7 g (53%). M. p. 171° (from ethyl alcohol).

Found %: C 68.83, 66.81; H 6.57, 6.58. $C_{13}H_{15}O_3N$. Calculated %: C 66.92; H 6.48.

1-Ethyl-2-methyl-3-carboethoxy-5-methoxyindole (II) (alternate synthesis). 2.3 g of 2-methyl-3-carboethoxy-5-methoxyindole (III) was dissolved in 20 ml of anhydrous alcohol. The resulting solution was mixed with an alcoholic solution of sodium alcoholate (50 ml of anhydrous alcohol and 2.3 g of sodium). To the solution obtained were added 10.9 g of ethyl bromide in 10 ml of anhydrous alcohol. The reaction mixture was heated for 1 hour on a water bath. Crystals of sodium bromide were separated out. The mother solution was left to evaporate at room temperature for two days. The crystals that precipitated (1.7 g) appeared to be the starting material 2-methyl-3-carboethoxy-5-methoxyindole. M.p. 161°. A mixed melting point test with the starting compound (III) gave no depression in melting temperature. The mother liquor was diluted with water.

Crystals that precipitated were separated out. Yield 0.5 g (19%). M.p. 67° (from methanol). A mixed melting point test with 1-ethyl-2-methyl-3-carboethoxy-5-methoxyindole (II) gave no depression.

1-Ethyl-2-methyl-3-carboethoxy-5-hydroxybenzindole (X). The reaction was carried out under the conditions used for the preparation of the indole (I). For the experiment 7.9 g of α-naphthoquinone, 11.5 g of the ethyl ester of N-ethyl-β-aminocrotonic acid, and 25 ml of dry acetone were taken. Yield 7.8 g (57%). M.p. 210° (from ethyl alcohol).

Found %: N 4.60, 4.69. $C_{18}H_{19}O_3N$. Calculated %: N 4.71.

Ethyl ester of N-cyanoethyl-β-aminocrotonic acid (IV). 53 g of β-aminopropionitrile and 86 g of acetoacetic ester were mixed. The reaction liquid was heated, while shaking, to 45°. The resulting solution was boiled for 5 hours and left over night. When 150 ml of ether was added to it, white crystals of (IV) precipitated. Yield 136 g (91.5%). M.p. 62° (from ethyl alcohol).

Found %: C 59.36, 59.35; H 7.88, 7.85. $C_9H_{14}O_2N_2$. Calculated %: C 59.31; H 7.74.

1-Cyanoethyl-2-methyl-3-carboethoxy-5-hydroxyindole (V). The reaction was carried out in the same way as for preparing (I), except that dichloroethane was used as the solvent. For the experiment 5 g of p-benzoquinone, 12 g of the ethyl ester of N-cyanoethyl-β-aminocrotonic acid (IV), and 25 ml of dichloroethane were taken. Yield of (V) 5 g (48%). M.p. 191° (from ethyl alcohol).

Found %: C 66.04, 65.85; H 6.11, 6.03. $C_{15}H_{16}O_3N_2$. Calculated %: C 66.17; H 5.92.

1-Cyanoethyl-2-methyl-3-carboethoxy-5-methoxyindole (VI). For the experiment 3 g of 1-cyanoethyl-2-methyl-3-carboethoxy-5-hydroxyindole (V), 18 ml of 2 N NaOH, and 3.3 g of dimethyl sulfate were taken. Yield of (VI) 3.5 g (quantitative). M.p. 135° (from ethyl alcohol).

Found %: C 67.26, 67.03; H 6.45, 6.20. $C_{16}H_{18}O_3N_2$. Calculated %: C 67.11; H 6.33.

2-Methyl-3-carboxy-5-methoxyindole (VII). 2 g of 1-cyanoethyl-2-methyl-3-carboethoxy-5-methoxyindole (VI) was dissolved in 10 ml of 50% solution of sodium hydroxide by heating. The mixture was heated for 20 minutes on a burner flame and then treated for 50 minutes with steam superheated to 270-280°. The aqueous solution, after evaporation to a small volume, was acidified with concentrated hydrochloric acid (to congo). Crystals of acid (VII) were separated. Yield 0.5 g (34%). M.p. 207° (from ethyl alcohol). A mixed melting point test with known compound [4] gave no depression.

Condensation of p-benzoquinone with N-methylimine of acetylacetone. To a solution of 2.5 g of p-benzoquinone with 10 ml of dichloroethane cooled with ice were added 4 g of N-methylimine of acetylacetone in 10 ml of dichloroethane. The reaction proceeded with spontaneous heating of the mixture. The solution was heated for 1 hour on a water bath. After gradual evaporation of the solvent the crystals that precipitated were recrystallized from alcohol. There was no nitrogen in the substance that was obtained. Yield 1.2 g (35%). M.p. 234-235°. A mixed melting point test with 2-methyl-3-acetyl-5-hydroxybenzofuran [1] gave no depression.

Condensation of p-benzoquinone with N-ethylimine of acetylacetone. The reaction was carried out as in the preceding instance. For the experiment 10 g of p-benzoquinone in 40 ml of dichloroethane and 17.9 g of N-ethylimine of acetylacetone were taken. 6.5 g (32.5%) of 2-methyl-3-acetyl-5-hydroxybenzofuran was obtained. M.p. 234° (from alcohol). A mixed melting point test with known compound [1] gave no depression.

SUMMARY

1. It has been shown that the condensation of p-benzoquinone with esters of N-ethyl- and N-cyanoethyl-β-aminocrotonic acid results in the synthesis of substituted indoles.

2. By the reaction of the N-methyl- and N-ethylimine of acetylacetone with p-benzoquinone only benzofuran derivatives are obtained.

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54. SYNTHESIS OF 1-ALKENYL-2,5-DIMETHYL-4-PIPERIDONES

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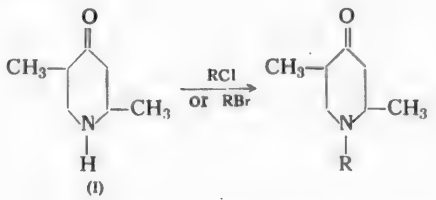
Continuing our investigations in the search for new anesthetics, we decided to synthesize various esters of γ-piperidols in the molecules of which there are unsaturated and chlorine-containing radicals of the allyl type attached to nitrogen. The effect of such substituents on the physiological activity of esters of γ-piperidols had not previously been studied. For the solution of the problem undertaken it was necessary for us first of all to prepare the corresponding γ-piperidones having the unsaturated and chlorine-containing substituents mentioned on the nitrogen. As representatives of such piperidones we selected 1-allyl-2,5-dimethyl-4-piperidone (II), 1-crotyl-2,5-dimethyl-4-piperidone (III), 1-(γ-chlorocrotyl)-2,5-dimethyl-4-piperidone (IV), 1-(γ,γ-dimethylallyl-2,5-dimethyl-4-piperidone (V), and also the piperidones (VI) and (VII), which contain substituents with conjugated diene and chlorodiene systems on the nitrogen.

The indicated piperidones (I-VII) were easily prepared in yields of 75-90% by heating the appropriate halogen derivatives of the allyl type with 2 moles of the available 2,5-dimethyl-4-piperidone (I) in benzene or dioxane solution.



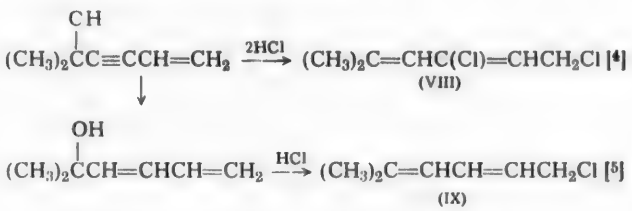
(I)

R = $CH_2CH=CH_2$ (II)
$CH_2CH=CHCH_3$ (III)
$CH_2CH=C(Cl)CH_3$ (IV)
$CH_2CH=C(CH_3)_2$ (V)
$CH_2CH=CH-CH=C(CH_3)_2$ (VI)
$CH_2CH=C(Cl)CH=C(CH_3)_2$ (VII)

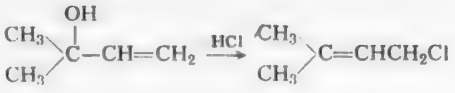
The second molecule of the 2,5-dimethyl-4-piperidone taken for the reaction is used up in combining with the hydrogen halide given off and is liberated again after processing, as also occurs in other alkylation reactions of this piperidone previously described [1, 2].

The starting compound 2,5-dimethyl-4-piperidone (I) was obtained by the reaction of ammonia or ammonium acetate with propenyl isopropenyl ketone, and also with the corresponding β-methoxyketones, which are produced by the addition to it of methanol [3].

The diene chlorides with conjugated double bonds (VIII) and (IX) were obtained by a method developed in our laboratory starting with dimethylvinylethynylcarbinol.



In a similar manner, γ,γ-dimethylallyl chloride was easily prepared by the action of hydrogen chloride on dimethylvinyl carbinol [6].



The 2,5-dimethyl-4-piperidones (II-VII) described in this report, which contain unsaturated substituents on the nitrogen, will be used for the synthesis of various esters of the corresponding piperidols for the purpose of comparative pharmacological investigations.

EXPERIMENTAL

1-Allyl-2,5-dimethyl-4-piperidone (II) [1]. To a solution of 14 g of 2,5-dimethyl-4-piperidone (I) (b.p. 78-80° at 11 mm) in 14 ml of dioxane was added 11 g of allyl chloride. The mixture was heated at 70° for 11 hours. The unreacted allyl chloride and dioxane were distilled off in vacuo and the residue was dissolved in 18 ml of water, treated with solid potassium hydroxide, extracted with ether, the ether extract dried with sodium sulfate, the ether distilled off, and the residue distilled in vacuo. 10.3 g of 1-allyl-2,5-dimethyl-4-piperidone was obtained:

B.p. 76° at 2 mm, n_D^{20} 1.4720, d_{20}^{20} 0.9464. MR_D 49.68; calc. 49.66.

1-Crotyl-2,5-dimethyl-4-piperidone (III). To a solution of 25.4 g of 2,5-dimethyl-4-piperidone (I) in 80 ml of dry benzene at 75-80° was added dropwise with continuous stirring 14 g of crotyl bromide, freshly distilled on a column, in 20 ml of dry benzene. After 20 minutes' heating a voluminous precipitate of the hydrobromide of the starting dimethylpiperidone (I) separated. The reaction mixture was heated for 1.5 hours and left overnight. The next day the precipitated hydrobromide of the starting dimethylpiperidone was filtered off, washed with dry benzene, the benzene distilled off on a water bath in a slight vacuum, and the residue distilled in vacuo with an oil pump. 16 g of 1-crotyl-2,5-dimethyl-4-piperidone (III) was obtained:

B.p. 87-89° at 2 mm, n_D^{20} 1.4761, d_4^{20} 0.9488, MR_D 54.18; calc. 54.28.
Found %: C 73.09, 72.81; H 10.61, 10.52; N 7.98, 7.99. $C_{11}H_{19}ON$. Calculated %: C 72.92; H 10.57; N 7.72.

A picrate was prepared by heating an alcohol solution of equimolar quantities of the piperidone (III) and picric acid for 1-2 minutes. It was a yellow, crystalline material with m.p. 145-147° (from alcohol).

Found %: N 13.78, 14.09. $C_{17}H_{22}O_8N_4$. Calculated %: N 13.65.

A hydrochloride was obtained by the action of hydrogen chloride on the piperidone (III) in dry ligroin After recrystallization from anhydrous alcohol it melted at 165-166°.

Found %: Cl 15.96, 15.73. $C_{11}H_{20}ONCl$. Calculated %: Cl 16.30.

The hydrobromide of the starting 2,5-dimethyl-4-piperidone, which was obtained along with the 1-crotyl-2,5-dimethyl-4-piperidone (III), was dissolved in water and treated with sodium carbonate; the base that separated was extracted with ether, dried with potassium carbonate, and distilled in vacuo. In this way 12 g of the starting piperidone (I) was isolated with b.p. 78-80° at 11 mm, n_D^{20} 1.4660.

1-(γ-Chlorocrotyl)-2,5-dimethyl-4-piperidone (IV). To a solution of 19 g of 2,5-dimethyl-4-piperidone (I) in 25 ml of dry dioxane was added dropwise a solution of 9.4 g of 1,3-dichlorobutene-2 (b.p. 123-126°) [7] in 15 ml of dioxane. The mixture was heated on a boiling water bath for 4 hours and left overnight. The next day the hydrochloride of the starting dimethylpiperidone that had precipitated was filtered off, the dioxane was distilled off, the residue was treated with water, extracted with ether, dried with potassium carbonate, and distilled in vacuo. 1.8 g of 1-(γ-chlorocrotyl)2,5-dimethyl-4-piperidone (IV) was obtained:

B.p. 111-113° at 2 mm, n_D^{20} 1.4950, d_4^{20} 1.0653, MR_D 58.99; calc. 59.15.
Found %: C 61.07, 60.94; H 8.50, 8.48; N 6.07, 6.28. $C_{11}H_{18}ONCl$. Calculated %: C 61.25; H 8.41; N 6.49.

Picrate – yellow crystals with m.p. 122-124°.

Found %: N 12.73, 12.34. $C_{17}H_{21}O_8N_4Cl$. Calculated %: N 12.61.

Hydrochloride – colorless crystals with m.p. 123-124.5° (from a mixture of anhydrous alcohol and anhydrous ether).

Found %: Cl(ionizable) 13.74, 13.58. $C_{11}H_{19}ONCl_2$. Calculated %: Cl (ionizable) 14.06.

1-(γ,γ-Dimethylallyl)-2,5-dimethyl-4-piperidone (V). To a solution of 50.8 g of 2,5-dimethyl-4-piperidone (I) in 50 ml of dry benzene at 70-75° was added with continuous stirring over a period of 30 minutes a solution of 27.2 g of freshly distilled γ,γ-dimethylallyl chloride [6] in 20 ml of dry benzene. The reaction mixture was heated for 4 hours and left overnight. The next day the hydrochloride of the starting 2,5-dimethyl-piperidone (I) that had precipitated was filtered off and washed on the filter with benzene (weight 32.2 g). After distilling off the benzene the product was distilled in vacuo. 35.5 g (91.2%) of 1-(γ,γ-dimethylallyl)-2,5-dimethyl-4-piperidone (V) was obtained:

B.p. 84-86° at 1 mm, n_D^{20} 1.4810, d_4^{20} 0.9371, MR_D 59.11; calc. 58.90.
Found %: C 73.63, 73.61; H 10.74, 10.95; N 7.13, 6.97. $C_{12}H_{21}ON$. Calculated %: C 73.86; H 10.76; N 7.18.

The hydrochloride of piperidone (V) was obtained by saturating an ether solution of the base with dry hydrogen chloride. After recrystallizing from a mixture of alcohol and ether it melted at 146-147°.

Found %: Cl 15.04, 14.86. $C_{12}H_{22}ONCl$. Calculated %: Cl 15.30.

The picrate of piperidone (V) formed yellow crystals with m.p. 138-139.5°.

Found %: N 13.31, 13.02. $C_{18}H_{24}O_8N_4$. Calculated %: N 13.21.

23.3 g of 2,5-dimethyl-4-piperidone (I) was recovered from the hydrochloride by the usual treatment; it boiled at 78-80° at 11 mm, n_D^{20} 1.4660.

1-(5-Methylhexadien-2,4-yl)-2,5-dimethyl-4-piperidone (VI). To 12.6 g of 2,5-dimethyl-4-piperidone (I) was added dropwise, with stirring, 6.8 g of 1-chloro-5-methylhexadiene-2,4- and the reaction mixture was heated at 60-65° for 6 hours. The precipitate of the hydrochloride of the starting dimethylpiperidone that separated was removed by filtration and the filtrate was acidified to congo with dilute hydrochloric acid (1 : 1), washed with ether, and then treated with potassium carbonate. The oil that came to the surface was repeatedly extracted with ether, dried with anhydrous sodium sulfate, and distilled in vacuo. 4.5 g of 1-(5-methylhexadien-2,4-yl)-2,5-dimethyl-4-piperidone (VI) was obtained with b.p. 119-120° at 2 mm; n_D^{20} 1.5105, d_4^{20} 0.9584, MR_D 69.20 (calc. 68.71). Yield 50%.

Found %: C 76.55, 75.82; H 10.56, 10.46; N 6.43, 6.10. $C_{14}H_{23}ON$. Calculated %: C 75.91; H 10.34; N 6.32.

The picrate of piperidone (VI) melted at 143-145° (with decomp).

Found %: N 12.29, 12.49. $C_{20}H_{26}O_8N_4$. Calculated %: N 12.30.

1-(3-Chloro-5-methylhexadien-2,4-yl)-2,5-dimethyl-4-piperidone (VII). To a solution of 38.1 g of 2,5-dimethyl-4-piperidone (I) in 20 ml of dry dioxane was added with stirring 54.4 g of 1,3-dichloro-5-methylhexadiene-2,4 and the reaction mixture was then heated at 60-65° for 3.5 hours and treated as in the preceding experiment. 23.3 g (61%) of 1-(3-chloro-5-methylhexadien-2,4-yl)-2,5-dimethyl-4-piperidone (VII) was obtained with b.p. 140-143° at 0.05 mm, n_D^{20} 1.5135.

Found %: C 65.19, 65.07; H 8.43, 8.37; N 5.43. $C_{14}H_{22}ONCl$. Calculated %: C 65.73; H 8.77; N 5.48.

Picrate – yellow crystals with m.p. 144-147° (with decomp).

Found %: N 10.93. $C_{20}H_{25}O_8N_4Cl$. Calculated %: N 11.55.

SUMMARY

By the reaction of 2,5-dimethyl-4-piperidone (I) with halogen derivatives of the allyl type, 75-90% yields

were easily obtained of the corresponding 2,5-dimethyl-4-piperidones (II-VII) which contain alkenyl radicals of the allyl type on the nitrogen.

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ALKYLACRIDONES AND THEIR TRANSFORMATIONS

II. PREPARATION OF 3-CHLORO-7-METHOXY-10-VINYLACRIDONE

B. I. Mikhantyev and V. A. Sklyarov

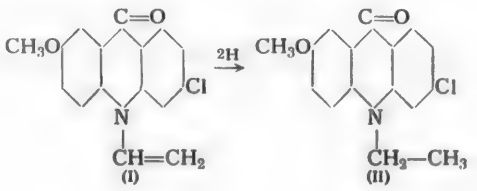
Continuing our studies in the field of investigation of vinyl derivatives of the acridine series [1], we have synthesized 3-chloro-7-methoxy-10-vinylacridone and studied some of its properties.

EXPERIMENTAL

Preparation of 3-chloro-7-methoxy-10-vinylacridone (I). 30 g of 3-chloro-7-methoxyacridone dissolved in 250 ml of isobutyl alcohol was vinylated [2] in a liter rotating autoclave in the presence of 5 g of powdered potassium hydroxide at 160-180° and an initial pressure of 18 atm. The vinylation was fully completed in 5-6 hours. The maximum pressure reached was 40 atm. It was established that acetylene reacts not only with 3-chloro-7-methylacridone but also with isobutyl alcohol. The latter forms vinyl isobutyl ether in good yield. Because of the lesser solubility of 3-chloro-7-methoxy-10-vinylacridone in vinyl isobutyl ether (in comparison with 3-chloro-7-methoxyacridone), it was obtained rather pure. Even in the crude condition it formed long, needle-shaped crystals of a lemon-yellow color with m.p. 230°. After recrystallization from benzene or alcohol the melting point of pure 3-chloro-7-methoxy-10-vinylacridone was 232°. The yield of the product was 31 g (95%).

Found %: N (oxidation with chromic mixture) 4.5; Cl (by Carius' method) 12.38. $C_{16}H_{12}O_2NCl$. Calculated %: N 4.91; Cl 12.42.

Determination of the structure of 3-chloro-7-methoxy-10-vinylacridone was carried out by reduction of this compound with hydrogen in the presence of skeletal nickel to a compound already known in the literature [3] 3-chloro-7-methoxy-10-ethylacridone (II).



2 g of 3-chloro-7-methoxy-10-vinylacridone dissolved in 200 ml of dioxane was reduced in the presence of 0.1 g of skeletal nickel. Hydrogenation was carried out by shaking at room temperature until the calculated amount of hydrogen had been added. The process was completed in the course of 6-7 hours. After the reduction the catalyst was filtered off and the 3-chloro-7-methoxy-10-ethylacridone obtained was precipitated from the filtrate with water.

3-Chloro-7-methoxy-10-ethylacridone (II) formed light-yellow, long needles, readily soluble in benzene, toluene, alcohol, dioxane, acetic acid, and other organic solvents. After recrystallization from alcohol it melted at 225°. The yield of 3-chloro-7-methoxy-10-ethylacridone was nearly theoretical.

Found %: Cl 12. $C_{16}H_{14}O_2NCl$. Calculated %: Cl 12.50.

SUMMARY

1. 3-Chloro-7-methoxy-10-vinylacridone has been prepared by the reaction of acetylene with 3-chloro-7-methoxyacridone.

2. It has been established that 3-chloro-7-methoxy-10-ethylacridone is produced by the reduction of 3-chloro-7-methoxy-10-vinylacridone with hydrogen in the presence of skeletal nickel.

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A HYDROCARBON $C_{12}H_{10}$ FROM THE ESSENTIAL OIL OF ARTEMISIA SCOPARIA W. K.

V. P. Golmov and N. M. Afanasyev

Continuing a study begun earlier [1] of the essential oils of various representatives of the genus Artemisia that grow in the Northern Caucasus, we have dealt in the present work with the essential oil of Artemisia scoparia W. K. ("venichnaya polyn, krasnobyl"). From the litereture we knew only the most important constants of this oil, which differed greatly among various authors [2-5].

The experiments that we carried out, which are described below, showed that hydrocarbons are the chief constituents of the essential oil of Artemisia scoparia. The most interesting was the very highest fraction of the essential oil, which was a mixture of two highly unsaturated hydrocarbons $C_{12}H_{12}$ and $C_{12}H_{10}$. Investigation of the first of them showed that it was apparently "agropyrene" (1-phenylhexen-2-yne-4), isolated previously by Treibs [6, 7] from the essential oil of the roots of Agropyrum repens.

The hydrocarbon $C_{12}H_{10}$, contained in the essential oil to the extent of about 27%, proved to be a compound undescribed in the literature. It could be separated from the agropyrene by the addition of bromine to the highest fraction of the essential oil, whereupon two bromides were produced – a liquid one, $C_{12}H_{12}Br_2$, and a crystalline one, $C_{12}H_{10}Br_4$.

Upon treatment with zinc dust and alcohol the liquid bromide gave agropyrene, and the crystalline one yielded the hydrocarbon $C_{12}H_{10}$. Both hydrocarbons upon treatment with bromine again yielded the starting bromides. This showed that isomerization did not occur on splitting out of the bromine and that the hydrocarbons obtained from the bromides were identical with those found in the essential oil.

The structure of the hydrocarbon $C_{12}H_{10}$ was demonstrated: a) by oxidation of it with an alkaline solution of $KMnO_4$ to produce benzoic, oxalic, and acetic acids; b) by catalytic reduction with the formation of 1-phenylhexane; and c) by ozonization, as a result of which there was ultimately produced phenylacetic, oxalic, and acetic acids.

On the basis of the experiments carried out we concluded that the hydrocarbon $C_{12}H_{10}$ was probably 1-phenylhexadiyne-2,4, i.e., it was "dehydroagropyrene" $C_6H_5-CH_2-C\equiv C-C\equiv C-CH_3$. This formula was not unexpected, since at that time there were already described in the literature more than thirty natural compounds with triple bonds, and there were also di- and polyynes among their number.

The first representative of the natural diynes was the so-called "lachnopyllum-ether" from the essential oil of Lachnopyllum gossypinum Bge, investigated in 1935 by one of us together with V. V. Vilyams and V. S. Smirnov [8]. Later a series of di- and polyynes was isolated from various plants and these belonged to the classes of esters [9, 10], alcohols [11-13], and hydrocarbons [13, 14].

The structure of the representatives of the group of compounds in question that had been isolated at that time was confirmed by synthesis [15-17]. Some of the natural compounds with triple bonds were antibiotics (micromycin [18], agrocibin [19], and an antibiotic from Clytocibe diatreta [20, 21]) or toxins (enantho- and cicutoxin [22]) and thus presented both theoretical and practical interest.

As shown by a preliminary microbiological study carried out at our request by M. I. Mamaichuk, professor of microbiology in the Pyatigorsky Pharmaceutical Institute, the hydrocarbon $C_{12}H_{10}$ also exerts a distinct antibacterial action.

EXPERIMENTAL

Samples of the essential oil were obtained by steam distillation of fresh, above-ground parts of plants collected in September in the amount of 175 kg on one occasion and 267 kg on another in the vicinity of the Sengilei-Stavropol border station. From the plants of the first collection 570 g of essential oil, i.e., 0.33%, was obtained; from the second collection 1052 g, i.e., 0.39%, was obtained. The essential oil was dried with calcined magnesium sulfate and filtered off from mechanical contaminants.

Investigation of the essential oil. The essential oil from Artemisia scoparia was a mobile liquid of dark brown color with a strong, characteristic odor. It had the following constants: d_4^{22} 0.9322, n_D^{22} 1.5349, acid no. 0, ester no. 0, ester no. after acetylation 0. The oil was insoluble in 20% alkali.

1442 g of the oil under investigation was subjected to fractional distillation in vacuo, and yielded the following fractions: 1st with b.p. 63-120° (25 mm), 448 g (31.0%); 2nd 121-146° (17 mm), 856 g (59.3%); residue (resinfied) 130 g.

Investigation of fraction with b.p. 63-120° at 25 mm. The fraction in question was separated by multiple distillations at ordinary pressure into 12 fractions with narrow boiling point ranges. The first two of these with b.p. 154-158° had d_4^{20} 0.8687, n_D^{20} 1.475 and $[\alpha]_D^{20}$ −11.9°. By oxidation of these with $KMnO_4$, pinonic acid was obtained with m.p. 101-102° (after redistillation in vacuo) [23]. The presence of α-pinene also was demonstrated by the formation of a nitrosochloride which after solution in chloroform and precipitation from the solution with methyl alcohol melted with decomposition at 102-103° [24].

In the following three fractions with b.p. 159-164° (d_4^{20} 0.868, n_D^{20} 1.477, $[\alpha]_D^{20}$ −20.2) β-pipene was found. As evidence of its presence a part of these fractions also was oxidized with permanganate and nopinic acid was obtained, melting at 126-127° (from benzene [25].

In the higher boiling fractions we were not able to identify the separate components by preparing crystalline derivatives. Part of the fractions with b.p. 165-180° was oxidized with $KMnO_4$ for the purpose of checking the presence of myrcene [4]; however we did not succeed in detecting succinic acid in the oxidation products.

Investigation of fraction with b.p. 121-146° at 17 mm. This fraction was subjected to repeated fractionation in vacuo with the result that there was isolated from it a substance with b.p. 101-103° at 1 mm in the amount of 72%; d_4^{22} 0.9755, n_D^{22} 1.5770.

Found %: C 92.43, 92.47; H 6.81, 6.61. M 154.9, 160. $C_{12}H_{10}$. Calculated %: C 93.46; H 6.49. M 154. $C_{12}H_{12}$. Calculated %: C 92.30; H 7.62. M 156.

When an attempt was made to distil the substance at atmospheric pressure, only a few drops distilled off at 255° and then the liquid suddenly boiled up violently with the formation of light yellow fumes and was converted into a black, brittle tar. For the purpose of purification from contaminants 20 g of the fraction with b.p. 101-103° was heated to boiling at 2 mm in an atmosphere of nitrogen with 0.8 g of metallic sodium. An explosion thereupon occurred that destroyed the apparatus.

Preliminary experiments indicated that the fraction with b.p. 101-103° instantly added bromine and reacted in the cold with a dilute solution of $KMnO_4$.

Addition of bromine to the fraction with b.p. 101-103°. To a solution of 30 g of the fraction in 100 ml of ether was added drop by drop, with cooling, 108 g of bromine. The next day part of the bromine still remained free. This was reduced with sodium sulfite solution, the ethereal solution was separated, washed, dried, and the solvent was distilled off. The residue quickly crystallized in part. After separation of the liquid and solid, 70 g (63.1%) of crystals and 25.2 g (34.4%) of a viscous, dark oil were obtained. The crystalline bromide after recrystallization from alcohol formed colorless, shining crystals with m.p. 62-62.5°.

Found %: C 30.80; H 2.17; Br 67.55, 67.27. M 493. $C_{12}H_{10}Br_4$. Calculated %: C 30.42; H 2.11; Br 67.47. M 474.

The liquid bromide had:

B.p. 176-178° (6 mm), d_4^{22} 1.5547, n_D^{22} 1.6060; MR_D 69.65. $C_{12}H_{12}Br_2$5 F. Calculated: 68.61. Found %: Br 49.52, 49.67. $C_{12}H_{12}Br_2$. Calculated %: Br 50.63.

Splitting out of bromine from the dibromide. 29 g of the dibromide, 50 ml of 60% alcohol, and 9 g of zinc dust were heated for 6 hours to 80° with mechanical stirring. After cooling, 50 ml of water was added, the liquid was extracted with ether, the ether extract was washed with water, dried with $CaCl_2$, and the ether distilled off. The residue was distilled in vacuo within the limits 140-142° at 10 mm.

d_4^{20} 0.9742, n_D^{20} 1.5665, MR_D 51.96 (calc. 51.55).
Found %: C 92.16; H 7.68. $C_{12}H_{12}$. Calculated %: C 92.30; H 7.69.
Constants for "agropyrene:" b.p. 140-143° (10 mm), d_4^{20} 0.9744, n_D^{20} 1.5695 [6].

Upon oxidation with an alkaline solution of $KMnO_4$, benzoic, oxalic, and acetic acids were obtained [6]. By catalytic hydrogenation in the presence of palladium on carbon 1-phenylhexane was produced, and by ozonization phenylacetic acid was obtained with m.p. 76-78°, the p-nitrobenzyl ester of which melted at 64-65°.

Splitting out of bromine from the tetrabromide. A mixture of 22 g of the tetrabromide with m.p. 62-62.5°, 12 g of zinc dust, and 50 ml of 60% alcohol were heated on the water bath with a reflux condenser to 80-85° for 1 1 hour. Further treatment was carried out as in the preceding experiment. The residue after distilling off the ether weighed 7 g (98%); it was distilled within the limits 100-101° at 1 mm or 123-124° at 5 mm.

d_4^{20} 0.9767; n_D^{20} 1.5810, MR_D 52.56 (calc. 51.97; exaltation for two conjugated triple bonds 1.96 [26]).
Found %: C 93.14; H 6.65. $C_{12}H_{10}$. Calculated %: C 93.46; H 6.49.

The substance added bromine, forming a crystalline tetrabromide with m.p. 62-62.5°. It did not give a crystalline compound with picric acid. It did not form copper or silver derivatives, which are characteristic of acetylenic compounds with a triple bond at the end of a chain.

Oxidation of the hydrocarbon $C_{12}H_{10}$ with potassium permanganate. The hydrocarbon obtained from the crystalline tetrabromide required 10 gram-atoms of oxygen per mole for oxidation. The products of the oxidation were benzoic and acetic acids and carbon dioxide; none of the starting hydrocarbon remained. Only when not more than 3 gram-atoms of oxygen per mole was used was it possible to detect oxalic acid also. This last experiment is described below.

15 g of the hydrocarbon was added to a solution of 36.4 g of $KMnO_4$ and 5 g of KOH in 875 ml of water. After a day the liquid was decolorized by the addition of methyl alcohol, the precipitate of manganese dioxide was separated off, and the filtrate and wash water was shaken with ether to remove unoxidized material (10 g of unoxidized hydrocarbon was recovered from the reaction). The liquid after extraction with ether was evaporated to a small volume and acidified with dilute sulfuric acid; upon this treatment a crystalline acid precipitated, weighing 4 g (theoretical 4.28 g). The substance sublimed, forming colorless plates with m.p. 122°, which did not give any depression in m.p. with benzoic acid.

Found %: C 68.22; H 4.88. $C_7H_6O_2$. Calculated %: C 68.85; H 4.92.

The mother liquor from the benzoic acid was treated with steam and a volatile acid passed over into the receiver. This was converted into the calcium salt (2.05 g), which was decomposed with sulfuric acid. Upon distillation 1.45 g of acetic acid was obtained (theoretical yield 2.1 g) with b.p. 115-120°. The p-nitrobenzyl ester melted at 77-78° [27].

The residue from the steam distillation was evaporated to a small volume and upon cooling 3.9 g (theoretical yield 4.5 g) of a nonvolatile acid separated. After recrystallization from water the substance melted at 100-101° and gave characteristic reactions for oxalic acid with calcium acetate, resorcinol and conc. H_2SO_4 [28], and $KMnO_4$.

0.0900, 0.0721 g of the substance required for titration 14.3, 11.5 ml of 0.1 N $KMnO_4$. Found $H_2C_2O_4 \cdot 2H_2O$: 0.0901, 0.0725 g.

Catalytic hydrogenation of the hydrocarbon $C_{12}H_{10}$. For each experiment we used 5 g of hydrocarbon obtained from the tetrabromide, 1 g of catalyst (palladium on carbon [8]), and 10 ml of dry ether. The experiment was ended when the quantity of hydrogen theoretically necessary for hydrogenation of two triple bonds had been added.

Upon vacuum distillation a substance was obtained with b.p. 95-96° at 8 mm or 217-219° at 710 mm.

d_4^{20} 0.8622, n_D^{20} 1.4892, MR_D 54.26. $C_{12}H_{18}3$. Calculated: 54.02.
Found %: C 88.65; H 11.32. $C_{12}H_{18}$. Calculated %: C 88.82; H 11.18.

Constants for 1-phenylhexane according to data in the literature [29]: b.p. 219-220°, d_4^{20} 0.8613, n_D^{20} 1.1900.

Ozonization of the hydrocarbon $C_{12}H_{10}$. 7.5 g of the hydrocarbon $C_{12}H_{10}$ was dissolved in 100 ml of dry chloroform and ozonized oxygen with an ozone content of about 3.5% was passed through the liquid. The gas was passed through at a rate of 300-400 ml per minute for 16 hours. The termination of the ozonization was determined when decolorization was not observed upon addition to a separate sample of bromine. The solvent was distilled off in vacuo at 25°, 150 ml of water was added to the remaining thick, viscous, brown mass and the liquid was boiled for 2 hours. By this treatment a large amount of tar was formed, which was separated mechanically, and the aqueous solution of the ozonization products was steam distilled. Acetic acid passed over into the receiver and was identified by conversion to its p-nitrobenzyl ester w th m.p. 77-78° (yield 2.1 g).

The liquid from the steam distillation was evaporated to dryness and the crystalline residue was fractionally crystallized from water. Part of the material more difficultly soluble in water was distilled in vacuo at 10 mm and boiled at 140-145° (yield 1.12 g). After recrystallization from water phenylacetic acid was obtained with m.p. 76-78° [30]. Its p-nitrobenzyl ester melted at 64-65° [27].

The fraction easily soluble in water appeared to be oxalic acid. After repeated recrystallization from water it melted at 100-101° (yield 0.8 g). The material gave positive qualitative reactions for oxalic acid (see under oxidation). It also was indicated by titration with potassium permanganate.

SUMMARY

1. The essential oil of Artemisia scoparia W. K. has been investigated and among its components have been found: α- and β-pinene (about 20%), "agropyrene," $C_{12}H_{12}$ (about 15%), and a hydrocarbon $C_{12}H_{10}$ not previously described (about 27%).

2. On the basis of a study of bromination, oxidation with alkaline potassium permanganate solution, catalytic hydrogenation, and ozonization it appears that the hydrocarbon $C_{12}H_{10}$ is probably 1-phenylhexadiyne-2,4 ("dehydroagropyrene").

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SYNTHESIS OF PTERIDINES FROM 4,5-DIAMINOPYRIMIDINES AND AROMATIC α-KETOACIDS

1. SYNTHESIS OF PTERIDINES FROM 4,5-DIAMINOPYRIMIDINES AND PHENYLPYRUVIC ACID

S. N. Baranov and T. E. Gorizdra

Compounds of the pteridine series were first prepared by Kuhling [1] and they were subsequently studied in more detail by Traube, Sachs, and Meyerheim, who called them azinepurines [2,3].

Later, compounds of this class were found in natural coloring matters. Thus, for example, a yellow pigment, xanthopterine, and a white pigment, leucopterine, were isolated from butterfly wings.

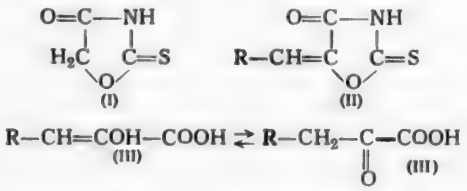
Since 1940-1941 this field of synthetic organic chemistry has been greatly developed, since it has been established that a number of growth factors of microorganisms and some of the supplementary factors for animal nutrition (vitamin B group) appear to be pterine derivatives. Thus, an important vitamin of this group, folic acid, contains the pteridine nucleus and p-aminobenzoic and glutamic acid groups. Folic acid has proved to be very effective in a serious form of anemia and also in blood disease developing after exposure to short waves; in experiments on animals the ability of substances of this group to inhibit the growth of cancerous tumors has been discovered [4-6].

The most prevalent method of preparing pteridines is the condensation of 4,5-diaminopyrimidines with dicarbonyl compounds [3, 7] or with monocarbonyl compounds containing halogen or a hydroxyl group in the α-position [8, 9].

There are also particular methods of preparing individual pteridines [10].

In the present work we used as carbonyl compounds aromatic α-ketoacids, which made it possible to prepare new derivatives of the pteridine series.

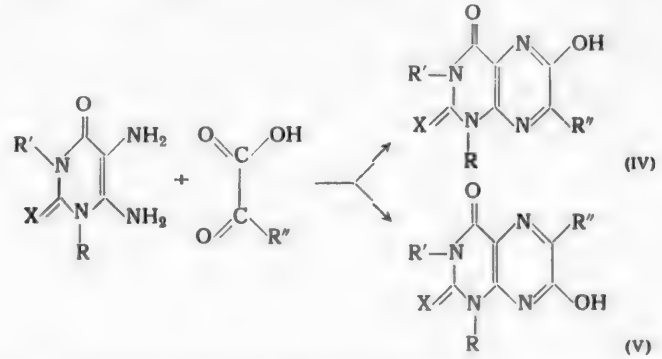
The aromatic α-ketoacids necessary for this purpose were obtained by a method developed in our laboratory [13], based on the hydrolysis of 5-arylidene-substituted 2-thionoxazolidone-4 (II). We obtained the latter by condensation of 2-thionoxazolidone-4 (I) with various aromatic aldehydes (and also with furfural) in acetic acid in the presence of anhydrous sodium acetate [11]. The 5-arylidene-2-thionoxazolidones-4 prepared in this way were subjected to alkaline hydrolysis with a solution of sodium or barium hydroxide, after which the arylpyruvic acids (III), which are difficultly soluble in water, were precipitated by acidification of the hydrolyzates.



The 5-arylidene-2-thionoxazolidones-4 and the arylpyruvic acids that they yielded on hydrolysis are shown in Table 1.

4,5-Diaminopyrimidines were prepared by the condensation of urea or its alkyl or aryl derivatives (also guanidine) with cyanoacetic acid, its ester or sodium salt [2, 12].

The pteridines were obtained by the condensation of 4,5-diaminopyrimidines with phenylpyruvic acids by prolonged refluxing of equimolecular quantities of these substances in 50 or 96% ethyl alcohol. The end of the reaction was determined by the absence of qualitative reaction of the pyrimidine with concentrated nitric acid. The reaction proceeded according to the following scheme



(IV)

(V)

where X = O or NH; R = H, CH_3, C_2H_5, C_6H_5; R′ = H, CH_3; R″ = $C_6H_5CH_2$.

As is seen from the diagram, formation of two products (IV) or (V) may result from the condensation. However, in our experiments we always obtained entirely homogeneous products which were not separated by chromatography on paper or on a column with aluminum oxide, i.e., only one of the possible isomers was formed. Considering that the NH_2 group in the diaminopyrimidine molecule in the 5 position has more basic properties [2], it may be assumed that acylation probably takes place in the 5 position and the keto group reacts with the NH_2 in the 4 position, i.e., the pteridine of formula (IV) is formed.

TABLE 1

Melting Points of 5-Arylidene-2-thionoxazolidones-4 and Arylpyruvic Acids

R	5-Arylidene-2-thionoxazolidones-4	Arylpyruvic acids	
		found	literature data
C_6H_5—	188°	156—157°	157°
o-ClC_6H_4—	170—171	150—151	152
$C_6H_5CH=CH$—	176	187—190	189—193
m-$NO_2C_6H_4$—	213	180	—
o-OHC_6H_4—	202	151	152—153
C_4H_3O-(фурил)—	231	129—130	131
p-$(CH_3)_2NC_6H_4$—	223	> 285	—
p-(OH)·m-$(OCH_3)C_6H_3$—	237—238	159—160	161

EXPERIMENTAL

Phenylpyruvic acid. To 10 g of 5-benzylidene-2-thionoxazolidone-4 was added 400 ml of 10% barium hydroxide solution and the mixture was boiled for 20 minutes. After cooling, 10% hydrochloric acid was added till an acid reaction. A white precipitate of phenylpyruvic acid separated. The product was recrystallized from benzene. M.p. 156-157°. Yield 6.67 g (83%).

Synthesis of 2,4,6-trihydroxy-7-benzylpteridine. 0.01 mole of 2,6-dihydroxy-4,5-diaminopyrimidine in 50% ethyl alcohol was heated in the presence of anhydrous sodium acetate (0.5-0.7 g) to boiling with 0.01 mole of phenylpyruvic acid until there was a negative test for pyrimidine with concentrated nitric acid (10-15 hours). The precipitate of 2,4,6-trihydroxy-7-benzylpteridine was purified by reprecipitation from dilute alkali solutions with hydrochloric or acetic acids, boiling alkaline solutions with carbon, and recrystallizing from 50% ethyl

alcohol. Yield 70-75%. The fine white crystals were insoluble in ether, benzene, chloroform, and 96% alcohol, poorly soluble in water, and readily soluble in glycol, ammonia, and alkalies. M.p. above 300°.

The synthesis of other pteridines was carried out in a similar manner with only the difference that aryl- and alkyldiaminopyrimidines were taken as the free bases and the condensation was carried out in 96% alcohol in the absence of sodium acetate. The pteridines obtained are shown in Table 2.

The ultraviolet absorption spectra* of the pteridines synthesized were determined with an SF-4 spectrophotometer. The solutions for taking the spectra were prepared by dissolving 0.01 g of pteridine in 1000 ml of 0.1 N NaOH; the thickness of the cell was 1 cm.

TABLE 2

Pteridine	R	X	R'	Yield (in %)	Melting point	Nitrogen content (in %)		Color of fluorescence
						found	calcu.	
(VI)	H	O	H	75 *	Above 300°	20.76	20.73	Dark blue - sky blue
(VII)	CH_3	O	H	80 *	Above 300	19.27	19.71	Dark blue - sky blue
(VIII)	CH_3	O	CH_3	85 *	205	18.26	18.78	Violet
(IX)	C_2H_5	O	H	65 **	268	18.80	18.78	Violet
(X)	C_2H_5	O	CH_3	70 **	209	17.07	17.94	Violet
(XI)	C_6H_5	O	H	75 **	Above 300	15.69	16.18	Violet
(XII)	C_6H_5	O	CH_3	60 **	Above 300	15.82	15.55	Violet
(XIII)	H	NH	H	68 **	Above 300	25.61	26.01	Sky blue

* Condensation conducted in 50% alcohol.
** Condensation conducted in 96% alcohol.

TABLE 3

Absorption Bands in Spectra of Pteridines

Pteridine	λ_{max} (in μ) (in mμ)	log ε	λ_{max} (in mμ)	log ε
(VI)	250, 279, 337	4.04, 3.98, 4.24	245, 270, 295	4.02, 3.96, 3.75
(VII)	250, 279, 338	4.02, 3.65, 4.14	240, 268, 290	3.97, 3.63, 3.51
(VIII)	280, 334	4.06, 4.34	260, 290	3.76, 3.88
(IX)	250, 275, 338	4.24, 3.88, 4.22	240, 270, 290	4.22, 3.85, 3.69
(X)	280, 333	3.79, 3.99	270, 295	3.61, 3.64
(XI)	265, 339	4.55, 3.94	230, 300	4.24, 3.55
(XII)	305, 355	4.44, 4.12	260, 335	4.15, 4.00
(XIII)	255, 345	4.25, 3.91	240, 300	4.20, 3.44

The characteristic absorption bands and the corresponding molecular extinction coefficients are given in Table 3.

As can be seen in the absorption curves given in Figures 1 and 2, the introduction of one methyl or ethyl group in position 1 of the pyrimidine nucleus does not cause a shift in the maxima of the absorption bands, but affects only the intensity of absorption (Curves VI, VII, X, Fig. 1). Introduction of a methyl group in position 3 of the pyrimidine nucleus with the presence in position 1 of a methyl or ethyl group causes not only a change in absorption intensity, but also a bathochromic shift of the absorption band at 275 mμ by 4-5 mμ and a hypsochromic shift of the absorption band at 338 mμ by 3-4 mμ (Curves VIII and X, Fig. 1).

Introduction of a phenyl group in position 1 of the pyrimidine ring causes a sharp increase in intensity of the absorption band at 250 mμ and a shift in it of 15 mμ to the direction of the long waves (Curve XI, Fig. 2).

Introduction of a methyl group in position 3 of the pyrimidine nucleus in the presence of a phenyl group in position 1 causes a significant bathochromic shift in the absorption bands; thus, the absorption band at 265 mμ is shifted by 40 mμ, and the absorption band at 339 mμ by 15-16 mμ.

* Spectra were taken by T. N. Gladyshevska.

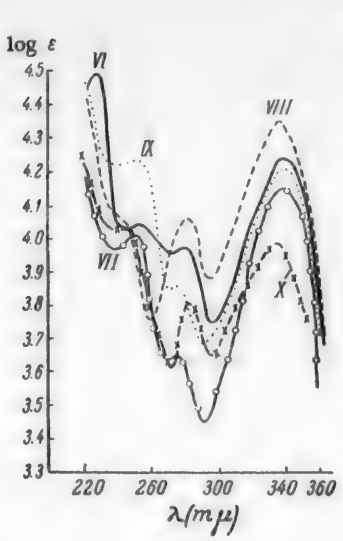


Fig. 1

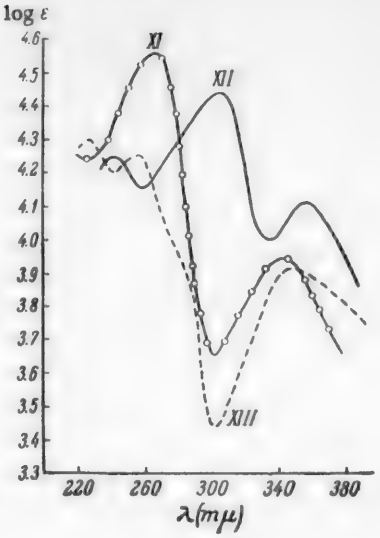


Fig. 2

Absorption spectra of pteridines in the ultraviolet region (numbers of curves correspond to numbers of pteridines in Tables 2 and 3).

It is interesting to note the closeness of the absorption spectra of the pteridine (XII), having a phenyl group in position 1 which attracts electrons, and pteridine (XIII), containing an NH− group in position 2 which repels electrons.

SUMMARY

1. A method has been proposed for the synthesis of arylpyruvic acids by alkaline hydrolysis of 5-arylidene-2-thionoxazolidones-4.

2. By the condensation of 4,5-diaminopyrimidines with phenylpyruvic acid 8 new pteridine derivatives were prepared and their ultraviolet absorption spectra were determined.

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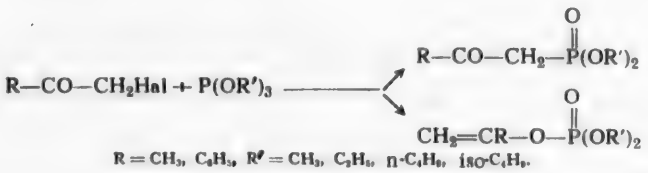
THE ANOMALOUS REACTION OF α-HALOKETONES WITH ESTERS OF PHOSPHOROUS ACID

V. REACTION OF HALO DERIVATIVES OF METHYL ETHYL KETONE AND ACETOPHENONE WITH TRIETHYL PHOSPHITE

A. N. Pudovik and L. G. Biktimirova

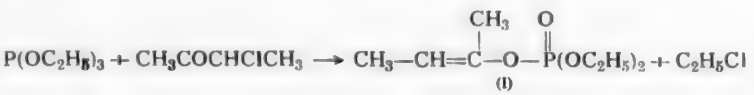
In our earlier investigations, it was shown [1] that the reaction of esters of phosphorus acid with primary α-haloketones proceeds simultaneously and independently in two directions: according to the Arbuzov rearrangement with the formation of esters of ketophosphonic acids and by an anomalous course with the formation of unsaturated esters of phosphoric acid.



The nature of the halogen and temperature at which the experiment is carried out both have a substantial effect on the ratio of the rates of these reactions. The transition from the iodo- to the bromo- and, further, to the chloroketone, and also a decrease in the temperature, promotes the reaction occurring by the anomalous mechanism [2].

As is well known, total esters of phosphorous acid react normally only with primary alkyl bromides. The reaction does not go with secondary bromides [3]. Splitting out of hydrogen bromide occurs with bromoallyl compounds with a secondary bromine atom, for example, with 2-bromo 3-pentene [4]. In this connection, it can be assumed that, other conditions being equal, the reaction of trialkylphosphites with α-haloketones containing a secondary halogen atom will proceed to a greater extent by the anomalous mechanism than does the reaction with monohalo derivatives of acetone and acetophenone. We chose methyl α-haloethyl ketones and bromocyclohexanone as objects of the present investigation.

Actually, on carrying out the reaction between triethylphosphite and methyl α-chloroethyl ketone, only one product – 1-methylpropenyl diethyl phosphate (I) – was obtained, and that in 70% yield.



The structure of (I) was proved by transesterification with ethyl alcohol and by ozonization. The products of the transesterification were identified as methyl ethyl ketone and triethyl phosphate. Ozonization gave acetaldehyde, which was identified as the dimedone derivative.

When the reaction was carried out between triethyl phosphite and methyl α-bromoethyl ketone, a mixture of (I) and methylphosphonoacetone (II) was obtained; the content of (I) was 90.7%. In the analogous reaction with bromoacetone, the isopropenyl ester of phosphoric acid comprised 80.1%. The difference in the ratio of products was considerably greater at elevated temperatures. At 110-130°, (I) comprised 81.2% of the mixture of (I) and (II), while in analogous reactions with bromoacetone and bromoacetophenone, the basic products are phosphonic acid esters [1]. We studied the rate of saponification of (I) and (II) in aqueous solution at 100°. As seen from the table (under Experimental), (I) saponifies considerably more rapidly than (II), which is in agreement with our previous data on the saponification of esters of phosphonic acid and unsaturated esters of phosphoric acid. The double bond content of (I) was determined by bromination according to the method of Mac Ilhiney; (II) does not contain a double bond. (II) has previously been prepared by one of us and N. M. Lebedeva by alkylation of the sodium derivative of phosphonoacetone with methyl iodide [5]. The data presented completely confirm the structures of (I) and (II). (I) and (II) were synthesized by B. A. Arbuzov and V. S. Vinogradova [6] in connection with a study of the tautomerism of phosphonoacetone and its homologs; the content of the enol form in (II) was determined by them by bromination according to the method of K. Meyer and by a spectroscopic method [7].

We isolated only the cyclohexenyl diethyl ester of phosphoric acid from the reaction of triethyl phosphite with α-bromocyclohexanone. The reaction with α-chlorocyclohexanone proceeds in an analogous manner. These results confirm our hypothesis concerning the effect of the position of the halogen in haloketones on the course of the reaction with phosphites. From the reaction of methyl α,α-dibromoethyl ketone with triethylphosphite was isolated, in 38% yield, only the 1-methyl-2-bromopropenyl diethyl ester of phosphonic acid (III). Considerable decomposition of the reaction mixture occurred during distillation of the reaction mixture, which did not permit completion of the distillation. Chlorination of (III) proceeded smoothly – the bromo-dichloro-sec-butyl diethyl ester of phosphoric acid was obtained in 92% yield.

$$P(OC_2H_5)_3 + CH_3COCBr_2CH_3 \longrightarrow CH_3CBr{=}C(CH_3){-}O{-}\underset{\text{(III)}}{\overset{\overset{O}{\|}}{P}}(OC_2H_5)_2 \xrightarrow{+Cl_2}$$

$$\longrightarrow CH_3CBrClCCl(CH_3){-}O{-}\overset{\overset{O}{\|}}{P}(OC_2H_5)_2$$

Further, we studied the reaction between triethyl phosphite and dichloroacetophenone, trichloroacetophenone, and tribromoacetophenone. With dichloroacetophenone and trichloroacetophenone, the reaction proceeded completely by the analogous mechanism; the 1-phenyl-2-chloroethyl [1-phenyl-2-chlorovinyl] diethyl ester of phosphoric acid (IV) and the 1-phenyl-2,2-dichloroethenyl [1-phenyl-2,2-dichlorovinyl] diethyl ester of phosphoric acid (V), respectively, were obtained in 80-90% yields. Chlorination of (IV) and (V) gave, respectively, the 1-phenyl-1,2,2-trichloroethyl diethyl ester and the 1-phenyl-1,2,2,2-tetrachloroethyl diethyl ester of phosphoric acid.

$$C_6H_5COCHCl_2 + P(OC_2H_5)_3 \longrightarrow CHCl{=}\underset{\text{(IV)}}{\overset{\overset{C_6H_5}{|}}{C}}{-}O{-}\overset{\overset{O}{\|}}{P}(OC_2H_5)_2$$

The 1-methyl-2,2-dibromoethenyl [1-methyl-2,2-dibromovinyl] diethyl ester of phosphoric acid was obtained, in small yield, by the reaction of triethyl phosphite with tribromoacetone; distillation was accompanied by considerable decomposition of the reaction mixture.

Finally, we investigated the reaction of triethyl phosphite with certain α,β-dihaloketones – with dichloro- and dibromobenzalacetone, 3,4-dichloro-2-hexanone, and 3,4-dichloro-4-methyl-2-pentanone. The liberation of ethyl chloride began on heating the reaction mixture to 100-150°. It was not possible to isolate the pure products of these reactions, since considerable tarring and decomposition of the reaction mixture occurred during distillation.

EXPERIMENTAL

Reaction of triethyl phosphite with methyl α-chloroethyl ketone. 43.4 g of triethyl phosphite was added dropwise to 26.4 g of methyl α-chloroethyl ketone heated to 90-100°. The temperature of the reaction mixture was gradually raised to 120°. The ethyl chloride distilled during the reaction. 35.3 g of the 1-methylpropenyl diethyl ester of phosphoric acid (I) was obtained by distillation of the reaction mixture.

B. p. 110-111.5° at 10 mm, d_4^{20} 1.0598, n_D^{20} 1.4274, MR_D 50.48; calc. 50.67.
Found %: P 15.29, 15.416. $C_8H_{17}O_4P$. Calculated %: P 14.89.

Transesterification of (I). To a solution of sodium ethylate, prepared from 0.2 g of Na and 15 ml of anhydrous alcohol, was added 10 g of (I). The mixture was heated on a water bath to distill the alcohol fraction, from which was precipitated 2.1 g of the semicarbazone of methyl ethyl ketone (m.p. 143°, mixed m.p. 145°). 5.5 g of triethylphosphate was obtained: b.p. 94-95° at 10.5 mm, d_4^{20} 1.0663, n_D^{20} 1.4065.

Ozonization of (I). Ozonized oxygen was passed into a solution of 4 g of (I) in 20 ml of dry carbon tetrachloride for a period of 18 hours. The ozonide was decomposed by heating with water, and the volatile products were distilled into a solution of dimedone. The condensation product of acetaldehyde with dimedone precipitated, m.p. 140°, mixed m. p. 141°.

Reaction of methyl α-bromoethyl ketone with triethyl phosphite. A mixture of 49.8 g of methyl α-bromoethyl ketone, 58.6 g of triethyl phosphite, and 100 ml of absolute ether was refluxed for 2.5 hours. The ether and the ethyl bromide formed during the reaction were distilled; the residue was distilled in a Widmer column. 36 g of the 1-methylpropenyl diethyl ester of phosphoric acid (I) and 5 g of methylphosphonoacetone (II) were obtained.

(I). B.p. 111.5-112° at 10 mm, d_4^{20} 1.0578, n_D^{20} 1.4272, MR_D 50.55; calc. 50.67.
Found double bond %: 79.1.
(II) B.p, 123-125° at 10 mm, d_4^{20} 1.0935, n_D^{20} 1.4340, MR_D 49.53; calc. 50.02.

Experiment II. 57.2 g of triethyl phosphite was added dropwise to 54 g of methyl α-bromoethyl ketone at 110°. The reaction mixture was heated at 130-140° for 4 hours. About 30 g of ethyl bromide distilled during the course of the reaction. Distillation of the residue gave 37.9 g of (I) and 8.8 g of (II).

Time from beginning of expt., hours	Amount of 0.01 N KOH required in titration (in ml)	
	Methylphosphonacetone (II)	1-Methylpropenyl diethyl phosphate (I)
2	2.1	3.7
3	2.8	5.3
5	4.5	9.7
7	5.2	13.4
8	5.7	14.9
10	6.8	18.4
11	7.4	19.1
13	8.3	22.8
14	8.7	24.5
16	9.6	28.3
20	14.0	39.8

Rate of saponification of 1-methylpropenyl diethyl phosphate and methylphosphonoacetone. The saponification was carried out in aqueous solution at 100° in glass ampoules. The concentration of the esters was 0.4 M. The acid esters formed were titrated with an 0.01 N solution of potassium hydroxide. The data are presented in the table.

The action of triethyl phosphite on bromocyclohexanone. Experiment I. To 20 g of triethyl phosphite, heated at 120°, was slowly added dropwise 14.6 g of bromocyclohexanone. The temperature of the reaction

mixture was maintained at the same level at all times during the addition. Distillation yielded 5.6 g of triethyl phosphite, 3.1 g of diethyl phosphite (b.p. 71-72° at 12 mm, n_D^{20} 1.4075), and 13.4 g of the cyclohexenyl diethyl ester of phosphoric acid (b.p. 144° at 12 mm n_D^{20} 1.4518, d_4^{20} 1.1033).

Experiment II. 19.5 g of bromocyclohexanone was gradually added to 20 g of boiling triethyl phosphite. 3 g of diethyl phosphite and 21.8 g of the cyclohexenyl diethyl ester of phosphoric acid (b.p. 147-148° at 15 mm, n_D^{20} 1.4524, d_4^{20} 1.1035) were obtained. Transesterification with ethyl alcohol in the presence of sodium ethylate gave cyclohexanone and triethyl phosphate.

Reaction of methyl α,α-dibromoethyl ketone with triethyl phosphite. 36.5 g of triethyl phosphite was added dropwise to 48 g of methyl α,α-dibromoethyl ketone. The temperature of the reaction mixture was maintained in the range of 20-30°. The ethyl bromide was then distilled on a water bath. Distillation of the residue yielded 22.8 g of the 1-methyl-2-bromopropenyl diethyl ester of phosphoric acid. The product tarred badly during distillation.

B.p. 147-148° at 10.5 mm d_4^{20} 1.3481, n_D^{20} 1.4655, MR_D 58.95; calc. 58.43.
Found %: Br 27.82, 27.45; P 10.94, 10.48. $C_8H_{16}O_4PBr$. Calculated %: Br 27.82; P 10.79.

Chlorination of the 1-methyl-2-bromopropenyl diethyl ester of phosphoric acid (III). While cooling with ice-salt mixture, chlorine was passed into a solution of 6.1 g of (III) in 20 ml of dry carbon tetrachloride until the theoretical weight increase was obtained (1.5 g). Distillation of the reaction mixture in a herringbone dephlegmator yielded 7 g of 1-methyl-2-bromo-2,3-dichloropropyl diethyl phosphate.

B.p. 164-165° at 10 mm, d_4^{20} 1.4677, n_D^{20} 1.4760, MR_D 68.84; Calc. 68.63.
Found %: 2Cl + Br 41.74, 41.84; P 8.86, 8.57. $C_8H_{16}O_4PCl_2Br$. Calculated %: 2Cl + Br 42.15; P. 8.65.

Reaction of α,α,α'-tribromoacetone with triethyl phosphite. To 55.4 g of molten tribromoacetone was added, dropwise, 32.7 g of triethyl phosphite. The temperature of the reaction mixture did not rise above 60°. Distillation in a Widmer column gave 7.1 g of the dibromoisopropenyl diethyl ester of phosphoric acid. The product decomposed badly during distillation.

B.p. 145-148° at 2.5-3 mm d_4^{20} 1.6340, n_D^{20} 1.4935, MR_D 62.64; calc. 61.58.
Found %: Br 45.1; P 8.33, 8.24. $C_7H_{13}O_4PBr_2$. Calculated %: Br 45.5; P 8.81.

Reaction of ω,ω-dichloroacetophenone with triethyl phosphite. 44 g of triethyl phosphite was added dropwise to 50 g of dichloroacetophenone. The temperature of the reaction mixture was maintained in the range of 20-30°. The ethyl chloride distilled during the course of the reaction. Distillation of the reaction mixture yielded 71 g of the 1-phenyl-2-chloroethenyl [1-phenyl-2-chlorovinyl] diethyl ester of phosphoric acid.

B.p. 139-140° at 0.5 mm, d_4^{20} 1.2353, n_D^{20} 1.5170, MR_D 71.30; calc. 70.41.
Found %: P 10.47, 10.80. $C_{12}H_{16}O_4PCl$. Calculated %: P 10.66.

Chlorination of the 1-phenyl-2-chloroethenyl diethyl ester of phosphoric acid. Chlorine was passed, while cooling, into a solution of 9.2 g of the phosphate in 20 ml of dry carbon tetrachloride until the theoretically required weight increase was obtained (2.25 g). Distillation of the reaction mixture yielded 6.2 g of the 1-phenyl-1,2,2-trichloroethyl diethyl ester of phosphoric acid.

B.p. 162-163° at 1 mm, d_4^{20} 1.3487, n_D^{20} 1.5149, MR_D 80.92; calc. 80.61.
Found %: Cl 28.76, 29.23; P 8.99, 9.36. $C_{12}H_{16}O_4PCl_3$. Calculated %: Cl 29.46; P 8.57.

Reaction of ω,ω,ω-trichloroacetophenone with triethyl phosphite. 39 g of triethyl phosphite was added dropwise to 47.6 g of trichloroacetophenone. The temperature of the reaction mixture was maintained in the range of 20-30. After distillation of the ethyl chloride, distillation of the reaction mixture yielded 53.8 g of 1-phenyl-2,2-dichloroethenyl diethyl ester of phosphoric acid.

B.p. 145-146° at 2 mm, n_D^{20} 1.5200, d_4^{20} 1.2945, MR_D 76.32; calc. 75.27.
Found %: P 10.18, 10.21. $C_{12}H_{15}O_4PCl_2$. Calculated %: P 9.54.

SUMMARY

1. It was shown that, in addition to the nature of the halogen and the temperature, the position of the halogen in α-haloketones has a substantial effect on the ratio of the rate of the reaction forming esters of

phosphonic acids to that of the reaction forming esters of phosphoric acids when α-haloketones are reacted with esters of phosphorous acid. α-Haloketones having a secondary halogen react anomalously with trialkyl phosphites to a significantly greater extent than do primary haloketones.

2. It was shown that the reaction of methyl α,α-dibromoethyl ketones, α,α,α'-tribromoacetone, and di- and triacetophenones with triethyl phosphite proceed anomalously with the formation of unsaturated esters of phosphoric acid.

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SYNTHESIS OF CERTAIN MERCAPTO DERIVATIVES OF PURINE

G. A. Garkusha

Mercapto derivatives of purine can be obtained from its halogen or hydroxy derivatives by the action of KSH (NaSH) or P_2S_5. 6-Mercaptopurine, a tumor-inhibiting medicinal preparation, has been synthesized from P_2S_5 and 6-hydroxypurine; tagged 6-mercaptopurine has been prepared from 6-chloropurine and $KS^{35}H$ [1].

The mercapto derivatives of purine described below were obtained by us from the corresponding halogen derivatives of purine and KSH (NaSH), as proposed by G.P. Menshikov. The basic raw material was 2,6,8-trichloropurine.

2,6,8-Trichloropurine was first prepared from 2,6-dichloro-8-hydroxypurine [2,3]. Later, it was obtained either by the action of a five-fold amount of $POCl_3$ on uric acid at 155-160°, the materials being heated in a sealed vessel over a period of 24-30 hours (yield 35-45%) [4], or by the action of a two-fold amount of $POCl_3$ on the Na, Mg, Ca, or Ba salt of uric acid under the same conditions but with a six-hour heating period [5]. Davoll and co-workers were unable to improve on these methods [6]; they prepared 2,6,8-trichloropurine from the ammonium salt of 2,6-dichloro-8-hydroxypurine and a 30-fold amount of $POCl_3$ in the presence of dimethylaniline (79%) yield). Later, Davoll and Lowy [7] proposed to react an 8-fold amount of $POCl_3$ directly with uric acid in the presence of dimethylaniline using a 20-hour heating period; the yield of the ammonium salt of 2,6,8-trichloropurine (after the first recrystallization) was 16-25%.

Checking the method of Davoll and Lowy [7], we were unable to improve it, since the initial uric acid does not dissolve completely, and the by-products of the reaction make separation and purification of the 2,6,8-trichloropurine difficult. We obtained 2,6,8-trichloropurine starting with the ammonium salt of 8-chloroxanthine, which, in turn, may be prepared, according to the data of Robins and Christensen [8], from acid potassium urate by the action of $POCl_3$ in the presence of triethylamine. The yield of 8-chloroxanthine is about 85%. The ammonium salt is obtained in about the same yield. During the interaction of the ammonium salt of 8-chloroxanthine with $POCl_3$ in the presence of dimethylamine, the salt completely dissolves, and the 2,6,8-trichloropurine is easily separated and purified. If one starts with 8-chloroxanthine itself or its potassium salt, the preparation of 2,6,8-trichloropurine is considerably more difficult.

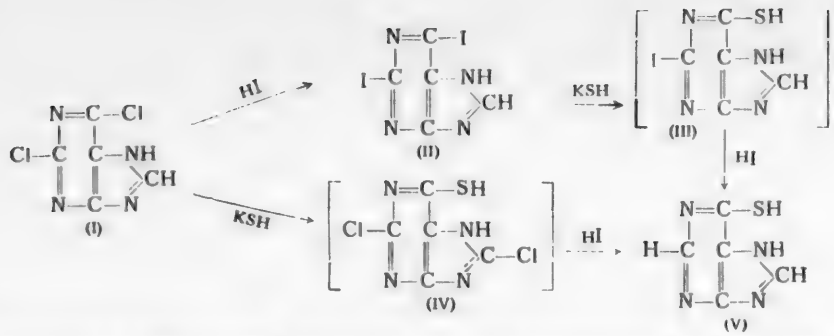
Starting with 2,6,8-trichloropurine and 2,6-dichloro-8-hydroxypurine, we obtained 2,6,8-trimercaptopurine and 2,6-dimercapto-8-hydroxypurine by heating with KSH under reflux; Fischer [9] carried out the heating in a sealed tube. Similarly, 2,6-dimercaptopurine has been obtained from NaSH and 2,6-diiodopurine [10].

Notwithstanding the indication of Fischer [9] to the effect that, in contrast to 7-methyl-2,6,8-trichloropurine, 2,6,8-trichloropurine does not form a mercapto derivative at room temperature, we were able to find conditions under which KSH will substitute a mercapto group into 2,6,8-trichloropurine and to obtain 6-mercaptopurine according to the scheme indicated below by using a reaction mixture containing HI(d 1.7), I_2, and P. However, the yield of 6-mercaptopurine was not high (about 11%). This substance was synthesized with better results from 2,6-diiodopurine (II) (see scheme).

EXPERIMENTAL*

2,6-Dichloro-8-hydroxypurine was prepared from 60 g of acid potassium urate and 60 ml of phosphoryl chloride by the method of Fischer. The yield was 25%.

* The 2,6-dimercapto-8-hydroxypurine and 2,6,8-trimercaptopurine were prepared with the assistance of E. Ya. Karaulova.



2,6-Dimercapto-8-hydroxypurine. 5.0 g of 2,6-dichloro-8-hydroxypurine was placed in a flask fitted with a reflux condenser and a dropping funnel and connected through a tee to a Tishchenko bottle containing water. After the addition of one 50 ml portion of a 1 N solution of KSH, the mixture was heated to 80°, and 100 ml of this same solution was added dropwise over a period of 3-4 hours. Completion of the reaction was established by the absence of halide in the reaction product; 5 ml of the reaction solution was collected, acidified with 10% H_2SO_4, the yellow precipitate separated, washed with water, and tested by the Beilstein test for halogen.* The product was salted out with sodium chloride from the filtered reaction solution after acidification with 10% sulfuric acid. The precipitate was mixed with 100 ml of water, heated to 50°, and alkalized with a 4% solution of $Ba(OH)_2$; the resulting solution was filtered with carbon, acidified with 10% HCl, the precipitate separated, washed with water, and dissolved in 80 ml of water by the addition of a 10% solution of Na_2CO_3 until the liquid was alkaline to phenolphthalein; this treatment was repeated. After drying at 105-110°, the weight of the material was 5 g.

The substance did not melt at temperatures up to 350°, and was difficultly soluble in alcohol and still more difficultly soluble in water.

Found %: N 27.99, 29.18; S 31.00, 30.66. $C_5H_4N_4OS_2$. Calculated %: N 28.0; S 32.0.

2,6,8-Trichloropurine. 24.5 g of the dry, carefully powdered ammonium salt of 8-chloroxanthine, 240 ml of freshly distilled $POCl_3$, and 35 ml of dry, distilled dimethylaniline were heated at 105-110° under reflux for about 6 hours until solution occurred. The excess $POCl_3$ was distilled under vacuum, and the viscous mass was poured onto ice (700 g); the precipitate was separated, pressed, washed with water, and dissolved in alcohol. The mother liquor was extracted with ether, and the resulting material was added to the main mass of product. The solvent was distilled from the acidic, filtered solution, which had been filtered with carbon, and the residue was dissolved in ether, filtered, and distilled. The residue was dissolved in 25 volumes of 5% ammonia while boiling, filtered, and the snow-white crystals which precipitated were filtered on the following day and carefully pressed and washed with ice water. The weight of the ammonium salt of 2,6,8-trichloropurine, after drying at 105°, was 13.5 g (46.6%, calculated on the original ammonium salt of 8-chloroxanthine). The 2,6,8-trichloropurine, which was obtained by acidification of a solution of this salt with HCl, had a m.p. of 177-180° (with intumescence). The yield was 11.0 g.

Found %: C 27.06, 27.17; H 0.88, 0.69. $C_5HN_4Cl_3$. Calculated %: C 26.82; H 0.45.

2,6,8-Trimercaptopurine. To 10 g of 2,6,8-trichloropurine was added a first 50 ml portion of a first 50-ml portion of a 1 N solution of KSH, and, while boiling on a water bath, another 450 ml was added over a period of 10 hours. After acidification with 10% H_2SO_4, the resulting precipitate was filtered, mixed with 500 ml of water, and alkalized at 50° with a 4% solution of $Ba(OH)_2$. The barium salt was salted out with NaCl, filtered, washed with water, mixed with 500 ml of water, and alkalized with a 10% solution of Na_2CO_3 to a pH of 8. After acidification with 10% H_2SO_4, a canary-yellow precipitate formed; this precipitate was washed with water, and dried at 105°. The weight was 5.0 g (51%). The substance did not melt at temperatures up to 350°, and was very difficultly soluble in water and in alcohol and other organic solvents.

Found %: N 25.76, 25.96; C 27.55, 26.61; H 1.28, 1.96. $C_5H_4N_4S_3$. Calculated %: N 25.92; C 27.77; H 1.85.

* In the preparation of the mercapto derivatives of purine described below, the same apparatus and the same method of taking the sample were used.

2,6-Diiodopurine. Beads, 60 ml of HI (d 1.7), and 20 g of powdered iodine were placed in a conical flask fitted with a stopper containing an outlet tube. After solution of the greater part of the iodine, 5 g of dry red phosphorus was added portionwise, with stirring, over a period of 10-15 minutes. If a sample of the mixture gave a violet color to benzene, the mixture was heated to 60°, and again tested for the presence of iodine. The mixture was cooled to 0°, and 10 g of a dry, ground 2,6,8-trichloropurine was added portionwise with stirring. The flask was closed with the stopper containing the tube, which was connected to a Tishchenko bottle, and carefully and continuously agitated while cooling to −3 to 0° (in the reaction mixture) over a period of 6-8 hours. On this same day, while cooling (with ice water), 120 g of ice was added portionwise with stirring, at which the temperature decreased to −15°. After melting of the greater part of the ice, a 12% solution of ammonia, cooled to 0°, was added portionwise with stirring until an alkaline reaction was obtained; during this procedure, the temperature in the flask was not permitted to rise above +15°. The red phosphorus was immediately separated, and washed with a 12% solution of ammonia; the precipitate was removed from the filter, mixed with a 12% solution of ammonia, and again filtered and washed with ammonia. The ammoniacal filtrates were combined, and immediately acidified with dilute HCl (1 : 2).

The crystalline precipitate was filtered on the following day, and washed with water, NaCl was added to the filtrate, and on the following day a few crystals were obtained. The product was mixed with 10 volumes of water, and alkalized with a 10% solution of Na_2CO_3. The solution was filtered with carbon, and acidified with HCl (as before) with subsequent filtration of the precipitate. After drying at 80°, the weight was 12.5 g, decomposition temperature 205-208° (with sublimation of iodine, carbonization and intumescence).

Found %: N 14.84, 15.03; C 16.47, 16.71; H 0.61, 0.52. $C_5H_2N_4I_2$. Calculated %: N 14.97; C 16.13; H 0.54.

2,6-Dimercaptopurine. 40 ml of a 1 N solution of NaSH was added to 3.75 g of 2,6-diiodopurine, and an additional 80 ml was added dropwise over a period of four hours while heating on a boiling water bath; the mixture was left on the water bath for an additional 1 hour or more, completion of the reaction being checked by means of samples collected from the mixture. After acidification of the filtered reaction solution with 10% H_2SO_4, a yellow solid was salted out with NaCl, washed with water, and mixed with 110 ml of water; on alkalizing with a 10% solution of Na_2CO_3, the solid dissolved, and the solution was filtered with carbon. The filtrate was acidified with 10% HCl, and the resulting precipitate was filtered, washed with water, and mixed with 200 ml of water; a 4% solution of $Ba(OH)_2$ was added at 60°, the barium salt salted out with NaCl and filtered and washed with ice water. The barium salt from the mother liquor was added to the main mass of material. The salt was mixed with 100 ml of water, and heated at 50° until it dissolved. The solution was filtered hot and with carbon, and the filtrate acidified with 10% HCl. The precipitate was dissolved in a 10% solution of Na_2CO_3 to give a solution of the sodium salt of 2,6-dimercaptopurine, as in the first case, and, after acidification with HCl, the desired reaction product itself was obtained. The weight was 1.8 g after drying at 105-110°. The material did not melt on heating to a temperature of 350°, and was very difficultly soluble in boiling water.

Found %: N 29.3, 29.7; S 35.94, 35.73. $C_5H_4N_4S_2$. Calculated %: N 30.4; S 34.8.

6-Mercaptopurine. a) Preparation from 2,6-diidopurine. I. 54 ml of a 10% solution of Na_2CO_3 was added in the cold to 18.0 g of 2,6-diiodopurine; 20 ml of a 1 N solution of KSH was then added, and this was followed by the addition of an additional 74 ml at 50-55° over a period of approximately 2 hours until the 2,6-diiodopurine dissolved. The reaction mixture was filtered, and the filtrate immediately acidified with 10% H_2SO_4. The yellow precipitate was filtered, washed, and mixed with 180 ml of water; a 10% solution of Na_2CO_3 was added to dissolve the precipitate (the Na_2CO_3 being added until the mixture was alkaline to bromothymol blue). The filtrate was acidified with 10% H_2SO_4, NaCl was added, and, on the following day, the precipitate was filtered and washed with ice water. The mercaptan product gave the usual qualitative reaction in the presence of iodine and sulfur, and had a decomposition temperature above 350°. The methyl derivative was prepared. 0.5 g of the material was mixed with 12 ml of water and dissolved by the addition of about 2 ml of 1 N NaOH (alkaline to phenolphthalein): 0.25 ml of CH_3I was added, and the solution was agitated for 30 minutes while adding portionwise 2 ml of NaOH solution; agitation was continued for another 1.5 hours, and the reaction mixture was then acidified with 5% acetic acid. After 24 hours, the white precipitate was separated and washed with water. The weight was 0.5 g (after drying at 80°). After two-fold recrystallization from a mixture of chloroform and methanol, the white crystals had a m.p. of 229-230° (with intumescence; the melt was brown).

II. To a reaction mixture prepared from 72 ml of HI (d 1.7), 24 g of iodine, and 12 g of red phosphorus, prepared as described for the preparation of 2,6-diiodopurine, was added portionwise and at room temperature 12.5 g of the dry, ground product from the mercaptanization of 2,6-diiodopurine, and the mixture was agitated for a half hour until a red-brown, homogeneous mass formed. The flask was then heated for half an hour on the water bath at 50° with periodic stirring. After cooling the reaction mixture to 0°, 140 g of ice was added portionwise, the temperature falling to −15°, and about 200 ml of a 12% solution of ammonia was added, as described for the preparation of 2,6-diiodopurine; the alkaline solution was separated from the phosphorus, and the residue washed with 12% ammonia. The combined filtrate was immediately acidified with 10% H_2SO_4, and a precipitate salted out with NaCl; the product was twice recrystallized from 100 volumes of boiling water. The water was evaporated from the mother liquor by heating at 50-60° under vacuum. After drying at 100-105°, the weight was 3.3 g (prismatic crystals) (yield 40% calculated on 100% 2,6-diiodopurine); decomp. temp. 310-314°.

Found %: C 35.33, 35.94; H 3.94, 4.10; N 32.4, 32.1. $C_5H_4N_4S \cdot H_2O$. Calculated %: C 35.3; H 3.5; N 32.9.

b) Preparation from 2,6,8-trichloropurine. I. To 5.5 g of anhydrous 2,6,8-trichloropurine and 10 ml of water was added, in the cold, 40 ml of a 1 N solution of KSH over a period of 10-15 minutes, and after heating to 55°, an additional 15 ml was added over a 20-minute period. After 1.5 hours, the reaction solution was rapidly filtered with carbon, and the filtrate was acidified with 10% H_2SO_4. The yellow precipitate was filtered on the following day, washed with water, and twice reprecipitated using a 10% solution of Na_2CO_3, as indicated above. The weight was 3.0 g (after drying at 80°).

The methyl derivative of the product, prepared as indicated above (Expt. I, a) had a m.p. of 249-250° (light yellow melt); on lowering the temperature, the material crystallized at 235-230°.

II. 4.0 g of the dry mercaptanization product was added portionwise to a reaction mixture prepared from 30 ml of HI (d 1.7), 15 g of iodine, and 4 g of red phosphorus, and the mixture was agitated with beads at room temperature for 1.5 hours. The mixture was heated at 50°, for not more than 30 minutes, until the reaction mass became red-brown. After cooling, 60 g of ice was added, and the reaction mixture decomposed with 12% ammonia, filtered, and acidified with 10% H_2SO_4, as indicated above. The crystals, recrystallized from water, weighed 0.5 g, m.p. 310-314° (after a second recrystallization from water).

6-Methylmercaptopurine. To a solution of 0.5 g of 6-mercaptopurine in 6 ml of water and 5.8 ml of a 1 N solution of NaOH, 0.85 g of CH_3I was added portionwise and with stirring over a period of 1 hour. An hour after stirring, the solution was acidified with 80% acetic acid; the precipitated needles, after 2-fold recrystallization from boiling water, melted at 217-218°.

Found %: C 42.67, 42.98; H 3.79, 3.86. $C_6H_6N_4S$. Calculated %: C 43.4; H 3.62.

We express our appreciation to A. D. Chinaeva and V. M. Rakova for carrying out the analyses.

SUMMARY

1. The preparation of 2,6,8-trimercaptopurine and 2,6-dimercapto-8-hydroxypurine is described. 2,6-Dimercaptopurine was prepared by a method which has not been described in the literature.

2. A synthesis, not described in the literature, is presented for 6-mercaptopurine.

3. A method, not described in the literature, is presented for 2,6,8-trichloropurine.

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SYNTHESIS OF PTEROYL-L (+) -GLUTAMIC ACID

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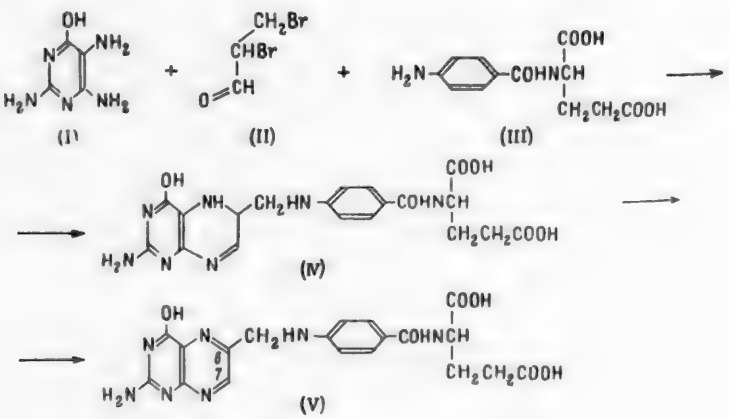
The compound frequently called folic acid, which is widely distributed in natural vitamin sources, was identified in 1946-1947 as pteroyl-L(+)-glutamic acid, N-{4-[(2-amino-4-hydroxy-6-pteridyl)-methyl]-amino}-benzoyl-L(+)-glutamic acid, and was subsequently synthesized [1]. Among the many methods for the synthesis of this compound [2], the single-step condensation of 2,4,5-triamino-6-hydroxypyrimidine (I) [3], 2,3-dibromopropionaldehyde (II), and p-aminobenzoyl-L(+)-glutamic acid (III) [4] is practical owing to its simplicity. Since during the formation of the pteridine ring and the alkylation of the aminobenzoylglutamic acid, three primary amino groups, differing in their reactivities, two halogen atoms, and an aldehyde group all enter into the reaction practically simultaneously, the condensation proceeds in more than one direction. One of the basic products of this condensation is pteroyl-L(+)-glutamic acid.

As shown by the synthesis of pteroyl-L(+)-glutamic acid using tagged dibromopropionaldehyde, the methylene bridge of the pteroylglutamic acid is formed from the $-CH_2Br$ group of the dibromopropionaldehyde [5]. That the intermediate dihydro form (IV) is formed is confirmed by the action of atmospheric oxygen in the



dehydrogenation to pteroylglutamic acid (V). Waller and co-workers [4] prepared pteroyl-L(+)-glutamic acid by this method with a yield of 7.1%; its optical antipode, pteroyl-D(−)-glutamic acid, was obtained in a nitrogen medium with a yield of 8.1% [6].

During the condensation of the three reacting substances, there also occurs the formation of isopteroylglutamic acid [7] – a compound in which the pteridine ring is joined to the methylene bridge and the rest of the molecule in the 7-position – 6-methylpterine (in the absence of dehydrogenating agents), the scource of which is dehydro-6-bromopterine formed by partial condensation, and other compounds. Instead of atmospheric oxygen, it is considerably better to use as dehydrogenation agents such substances as potassium or sodium dichromate [8, 9], mercuric acetate [10], and iodine in the amount of ½ equivalent [11-13]. The latter oxidizing agent was used by O. Yu. Magidson and K. A. Chkhikvadze in the All-Union Scientific Research Chemical-Pharmaceutical Institute for the preparation of pteroylglutamic acid [14].

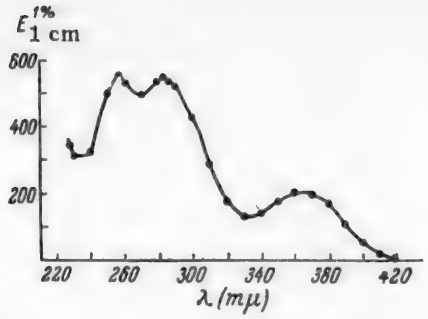


Fig. 1. Absorption spectrum of pteroyl-L(+)-glutamic acid (recrystallized from water) in 0.1 N NaOH.

The fact that the reaction is not unidirectional, the change in the reactivities of the reacting groups and atoms with a change in hydrogen ion concentration, and other factors increase the difficulty of obtaining reproducible results in the synthesis of pteroylglutamic acid.

In the present work, we studied the influence of the various factors (temperature, pH, composition of the medium, and others) on the yield of pteroyl-L(+)-glutamic acid from this reaction in the presence of iodine. Under optimum conditions, the yield of pteroyl-glutamic acid was 23%.

The resulting raw pteroyl-L(+)-glutamic acid was purified by reprecipitation from concentrated hydrochloric acid [15]. Considerably better results were obtained by a method developed by us in which the acid is reprecipitated from partially diluted hydrochloric acid (7 N) with subsequent dilution with water (to 1-1.6 N) to liberate the pteroylglutamic acid. The yield of pteroylglutamic acid from this purification method amounted to 70%; product purity was 94%.

By reprecipitation from hydrochloric acid, in addition to separation from insoluble pteridine compounds, the pteroylglutamic acid is purified from isopteroylglutamic acid, which is very unstable and readily undergoes cleavage both in alkaline and in acid solutions [7].

The absorption spectrum of pteroyl-L(+)-glutamic acid in the ultraviolet region has three maxima: λ 256, 282, and 365 mμ (Figure 1).

EXPERIMENTAL

Condensation of p-aminobenzoyl-L(+)-glutamic acid, 2,4,5-triamino-6-hydroxypyrimidine, and 2,3-dibromopropionaldehyde. To an enameled reactor were charged 1.8 liters of water, 41 g of 2,4,5-triamino-6-hydroxypyrimidine dihydrochloride [6], 50 g of p-aminobenzoylglutamic acid (crystalline) with a m.p. of 171-172°, 32 g of potassium iodide (the starting materials were calculated on the basis of 100% purity), and the mixture was stirred; all went into solution. The solution was then heated to the predetermined temperature (20-50°), 200-250 ml of 1 N sodium hydroxide was added to obtain the desired pH (from 2.4 to 4.8), and, with stirring, a solution of 40.6 g of dibromopropionaldehyde (b.p. 60-61.5° at 7 mm), 24 g of crystalline iodine (½ equivalent), and 14.5 g of potassium iodide in 1.0 liter of ethyl, isopropyl, or other alcohol was gradually added. 800-900 ml of 1 N sodium hydroxide was simultaneously added at a rate such that the pH of the medium was in the specified range (2.4-4.8). The addition of the alcoholic solution of dibromopropionaldehyde and of the sodium hydroxide solution was carried out over a period of 1.5 hours with frequent periodic measurement of the pH. After the addition of the entire amount of dibromopropionaldehyde and of the required amount of sodium hydroxide solution, the reaction mixture was stirred for 1.5-2 hours at this same temperature and pH. At the end of this time, the pH of the solution was brought to 3.1-3.2 by the addition of a 1 N solution of hydrochloric acid or sodium hydroxide. The reaction mixture was then cooled to 15°, the pteroylglutamic acid filtered, repeatedly washed with water and then with alcohol, and dried.

Purification of the 15-35% raw pteroylglutamic acid was carried out by the method of Waller [15] by reprecipitation from a 20-fold amount (with respect to 100% pteroylglutamic acid) of concentrated hydrochloric acid (10-10.5 N). Both the raw and the purified pteroylglutamic acid were subjected to chemical analysis [16].

The dependence of the yield of pteroylglutamic acid on temperature and on hydrogen ion concentration, when using isopropyl alcohol as the solvent, was studied in a series of experiments, the results of which are presented in Figures 2-4.

At a pH of 2.4-4.8, a reaction temperature of 30° was preferable to 40°. A reaction temperature of 50° gave especially poor results in the pH range 4-4.8. The optimum pH range was 3.2-4.0, preferably close to 3.6. The predominant formation of isopteroylglutamic acid occurred at 20° and a pH of 2.4-3.2, as is indicated by the lower yield after purification (isopteroylglutamic acid was included in the results of the analyses for

pteroylglutamic acid, but it decomposed in the strongly acid medium during purification).

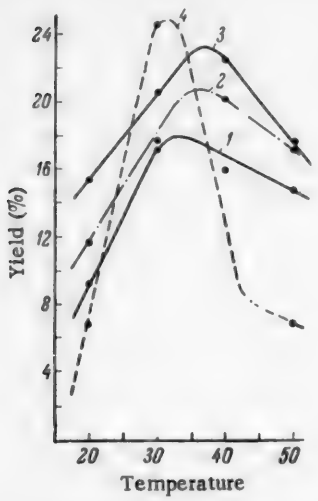


Fig. 2. Dependence of the yield of raw pteroyl-L(+)-glutamic acid on experiment temperature at various pH values.
pH values: 1) 2.4, 2) 3.2, 3) 4.0, 4) 4.8.

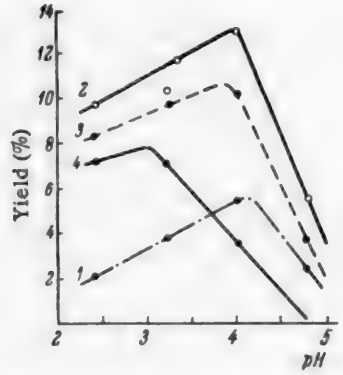


Fig. 4. Dependence of the yield of purified pteroyl-L(+) glutamic acid on pH at various temperatures.
1) 20°, 2) 30°, 3) 40°, 4) 50°.

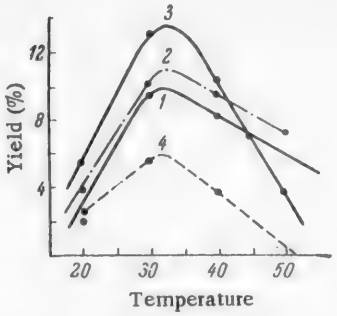


Fig. 3. Dependence of the yield of purified pteroyl-L(+)-glutamic acid on experiment temperature at various pH values.
pH values: 1) 2.4, 2) 3.2, 3) 4.0, 4) 4.8.

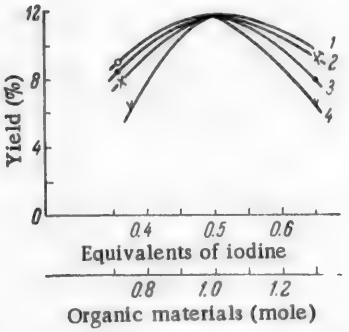


Fig. 5. Dependence of the yield of purified pteroyl-L(+)-glutamic acid on the ratio of starting materials.
1) 2,4,5-triamino-6-hydroxypyrimidine,
2) p-aminobenzoylglutamic acid, 3) iodine,
4) 2,3-dibromopropionaldehyde.

The dependence of the yield of pteroylglutamic acid on the ratio of the reacting substances was studied in a series of experiments, the results of which are presented in Figure 5. The temperature of the experiments was 38-40°; the pH 3.8-4.0.

A variation in the amount of one of the three reacting substances (p-aminobenzoylglutamic acid, 2,4,5-triamino-6-hydroxypyrimidine, and 2,3-dibromopropionaldehyde) from equimolar, either an increase or a decrease, led to an almost proportional change in the yield. This was also observed in the case of iodine (with reference to ½ equivalent). The experiments were carried out at a pH of 3.8-4.0 and a temperature of 38-40°.

The yields of pteroylglutamic acid definitely depended on the character of the aliphatic alcohols used as the solvent for dibromopropionaldehyde and which formed a part of the composition of the alcohol-water medium. The best results were obtained with ethyl and iso- and n-propyl alcohols (Table 1).

TABLE 1

Alcohol forming part of the composition of the medium for the condensation	Yield of pteroylglutamic acid (in %)	
	Raw	Purified
Methyl	16.9	9.7
Ethyl	21.6	11.9
Isopropyl	20.6	13.0
n-Propyl	20.6	13.2
Isobutyl	16.9	7.7

TABLE 2

Comparative Experiments on the Purification of Raw Pteroylglutamic Acid

Content of pteroylglutamic acid in raw product (in %)	Purified pteroylglutamic acid (in % of original 100% material) when using	
	Concentrated hydrochloric acid (10.5 N)	Diluted hydrochloric acid (7.1 N)
29.7	31.6	52.0
35.9	47.6	70.5
25.5	34.0	48.6
25.4	35.0	49.4
25.2	40.9	65.7

Purification of raw pteroylglutamic acid by reprecipitation from diluted hydrochloric acid. 18 g of powdered raw pteroylglutamic acid (recalculated to 100%) was dissolved in 120-150 ml of diluted (2:1) hydrochloric acid (7.1 N) while cooling to 5-8°; the solution was then stirred for 20 minutes with 5 g of activated carbon, and filtered. The carbon was washed on the filter with 36 ml of 7.1 N hydrochloric acid. The resulting filtrate (180 ml) was diluted with 720-750 ml of water (to 1.6 N), and allowed to stand for several hours. The purified pteroylglutamic acid precipitated during this time; it was filtered, washed with distilled water and alcohol, and dried under vacuum. 13.5 g of pteroylglutamic acid was obtained with a content of 93.8%, which corresponded to 12.65 g of 100% acid. Table 2 presents comparative data on the purification of various samples of raw pteroylglutamic acid by reprecipitation from 10.5 N and from 7.1 N hydrochloric acid.

SUMMARY

1. The relationship between the yield of pteroyl-L(+)-glutamic acid by the condensation of p-aminobenzoylglutamic acid, 2,4,5-triamino-6-hydroxypyrimidine, and 2,3-dibromopropionaldehyde and pH of the medium, temperature, amounts of reacting substances, and other factors was studied.

2. The method of purification of pteroylglutamic acid was improved.

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REACTIONS OF HYDRAZINE DERIVATIVES

XIV. A NEW METHOD OF SYNTHESIS OF 3-ALKYLPYRAZOLINES

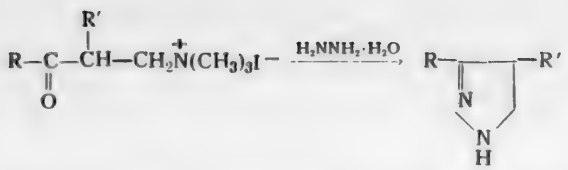
A. N. Kost and V. V. Ershov

Previously, we developed a new method for the synthesis of 3-aryl- and 3-aryl-4-alkyl pyrazolines based on the interaction of hydrazine with various β-dialkylaminoketones of the aromatic series [1-3]. Aminoketones in the form of the hydrochlorides were used by us for the synthesis of pyrazolines, and the reaction was carried out in the presence of alkali and excess hydrazine.

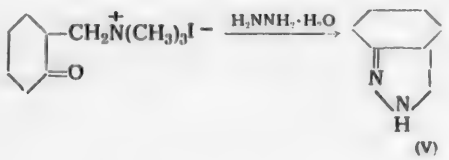
In an attempt to extend the reaction to β-dialkylaminoketones of the aliphatic series, it developed that these compounds, used in the form of the free base, do not readily split out the amino group to form the corresponding pyrazoline, and under ordinary conditions, they give only the hydrazones of the original aminoketones. Thus, for example, 4-dimethylamino-2-butanone (I) on reaction with hydrazine hydrate gives a stable hydrazone which can be distilled under vacuum. The action of concentrated hydrochloric acid on this hydrazone results in the splitting out of hydrazine, and benzaldehyde azine is formed in quantitative yield by the action of benzaldehyde. Both of these reactions are typical of hydrazones, but are not characteristic of pyrazolines. An attempt to obtain a pyrazoline by heating the hydrazone of the aminoketone (I) was unsuccessful, since the splitting out of dimethylamine begins at a temperature of about 170°, at which 3-methylpyrazoline itself is unstable. After boiling for 2.5 hours in the presence of sodium ethylate, 4-dimethylamino-2-butanone hydrazone was recovered unchanged.

This difference in the behavior of aminoketones of the aliphatic and aromatic series can be explained as follows. According to the data of Nisbet [4], who investigated in detail the reaction between aromatic β-dialkylaminoketones and phenylhydrzaine, the formation of 1-phenylpyrazolines proceeds through the intermediate stage of the phenylhydrazone of the corresponding unsaturated ketone. In those cases where it is impossible for a dialkylamine to split out with the formation of a double bond, as in the case of, for example, β-dimethylamino-α,α-dimethylpropiophenone, the reaction with phenylhydrazone does not go [5]. It is well known that the splitting out of an amino group from β-aminoketones proceeds by an ionic mechanism [6]. In the present case, it can be assumed that the benzene ring in aromatic ketones weakens the polarizing effect of the carbonyl group (orienting group of the second type) or, what amounts to the same thing, of the hydrazone group, relatively increasing the electron density at the α-carbon atom of the aminoketone and thereby promoting the splitting out of the amino group by an ionic mechanism. As was shown previously by us [2], the presence of an orienting group of the second order in the aromatic nucleus of an aminoketone decreases the yield of the pyrazoline during the reaction with hydrazone; hence, it is evident that the effect of the aromatic nucleus is neutralized to an appreciable extent by the effect of the substituent. In aliphatic β-aminoketones, specifically in 4-dimethylamino-2-butanone in which a methyl group replaces the aromatic nucleus, there is no such effect; the α-carbon atom is poor in electrons, and splitting out of dimethylamine under the influence of hydrazine is difficult.

In order to facilitate splitting out of an amino group, it is necessary to convert it to the quaternary ammonium salt [7]; the positively charged nitrogen attracts electrons, the amino group splits out. Thus, by reacting with hydrazine various β-dimethylaminoketones of the aliphatic series in the form of their quaternary salts (methiodides) we obtained a number of pyrazolines having substituents of the 3- and 4-positions depending on the structure of the aminoketone used. However, the yields of these pyrazolines were considerably lower than in the aromatic series.



The reaction proceeds in methyl alcohol with slight evolution of heat. We prepared by this method 3-methylpyrazoline (II, R = CH_3; R' = H) in 30% yield, 3-tert-butylpyrazoline (III, R = $(CH_3)_3C$; R' = H) in 48% yield, 3-ethyl-4-methylpyrazoline (IV, R = C_2H_5; R' = CH_3) in 42% yield. Cyclic ketones behave similarly in this reaction. Thus, 3,4-tetra-methylenepyrazoline (V) was obtained in 38% yield from the methiodide of 2-dimethylaminomethyl-1-cyclohexanone.



(V)

All pyrazolines were isolated as the free bases, and characterized by solid derivatives. These substances were unstable in the presence of atmospheric oxygen, but can be stored in an atmosphere of nitrogen.

The original β-dimethylaminoketones were prepared from the corresponding ketones by Mannich reaction. This reaction is usually carried out using aqueous solutions of a secondary amine or formaldehyde. We carried out the condensation of ketones with dimethylamine hydrochloride and solid paraformaldehyde either in the presence of alcohol as a solvent or in the absence of a solvent. Under these conditions, good yields of β-dimethylaminoketones were obtained. Thus, we obtained 4-dimethylamino-2-butanone (I), in 45.6% yield, 5-dimethylamino-2,2-dimethyl-3-pentanone (VI) in 77.4% yield, 1-dimethylamino-2-methyl-3-pentanone (VII) in 68% yield, and 2-dimethylaminomethyl-1-cyclohexanone (VIII) in 60.2% yield. All of these aminoketones were very stable, and readily distilled under vacuum in a stream of nitrogen. With methyl iodide in absolute ether, they gave the methiodides, which crystallized readily from anhydrous alcohol.

It is indicated in the literature that the methiodide of aminoketone (VIII) solidifies again at 160° after melting (152-153°) [8]. We observed this phenomenon with all of the methiodides prepared by us, the second solidification depending to an appreciable extent on the rate at which the temperature was raised. The second melting point was approximately the same for all of the methiodides, and lay in the range 258-261°, which corresponds to the melting point of trimethylamine hydriodide [9]. Evidently, during melting of the methiodide of an aminoketone, trimethylamine hydriodide is split out causing solidification of the mixture and later melting at its normal melting point.

EXPERIMENTAL

4-Dimethylamino-2-butanone (I). A mixture of 100 ml of acetone, 14 g of finely powdered paraformaldehyde, and 32 g of dimethylamine hydrochloride was refluxed 7 hours. The excess acetone was distilled, and the residue was made alkaline in ether, first with a 40% solution of sodium hydroxide and then with the solid alkali. The free base was extracted 3 times with ether; the extract was dried with potassium carbonate, and distilled under vacuum in a stream of nitrogen. The yield was 21 g (45.6%).

B.p. 72-74° (40 mm), n_D^{20} 1.4240, d_4^{20} 0.8723, MR_D 33.72; calc. 33.86.
Literature data [10]: b.p. 70° (40 mm), n_D^{25} 1.4213, d_4^{25} 0.8636.

The methiodide was obtained with a yield of 92% by the addition of methyl iodide to the aminoketone dissolved in absolute ether. It melted at 167° (from anhydrous alcohol), and immediately solidified; second m.p. 261°.

5-Dimethylamino-2,2-dimethyl-3-pentanone (VI). A mixture of 60 g of pinacolone, 56 g of dimethylamine hydrochloride, 20 g of paraformaldehyde, 1 ml of concentrated hydrochloric acid, and 30 ml of alcohol was refluxed with mechanical stirring for 4.5 hours. The mixture was cooled, made alkaline, and the aminoketone isolated similarly to the preceding. The yield was 72 g (77.4%).

B.p. 74-75° (14 mm), n_D^{20} 1.4311, d_4^{20} 0.8569, MR_D 47.59; calc. 47.71.
Found %: C 68.73, 68.86; H 12.16, 12.20. $C_9H_{19}ON$. Calculated %: C 68.74; H 12.18.

The methiodide, obtained in 85% yield, melted at 196° (from anhydrous alcohol), and then immediately solidified; second m.p. 260°.

Found %: N 4.88, 4.73. $C_{10}H_{22}ONI$. Calculated %: N 4.68.

1-Dimethylamino-2-methyl-3-pentanone (VII). A mixture of 86 g of diethyl ketone, 94 g of dimethylamine hydrochloride, and 35 g of paraformaldehyde was refluxed with stirring for 1 hour. The aminoketone was isolated by the usual method. The yield was 97 g (68%).

B.p. 59-61° (11 mm), n_D^{20} 1.4286, d_4^{20} 0.8579, MR_D 43.10; calc. 43.09.
Found %: C 67.17, 67.34; H 11.93, 11.90. $C_8H_{17}ON$. Calculated %: C 67.09; H 11.97.

The methiodide was formed very much more slowly than in the case of the preceding ketones. The yield was 80%; it melted at 155° (from anhydrous alcohol), and then gradually hardened; second m.p. 258°.

Found %: N 5.13, 5.09. $C_9H_{20}ONI$. Calculated %: N 4.91.

2-Dimethylaminomethyl-1-cyclohexanone (VIII). A mixture of 98 g of cyclohexanone, 81 g of dimethylamine hydrochloride, 35 g of paraformaldehyde, and 40 ml of alcohol was heated to boiling. The reaction then proceeded with the vigorous evolution of heat, and cooling was required. After completion of the reaction, the mixture was refluxed for 15 minutes and the aminoketone was isolated by the usual method. The yield was 92 g (60.2%).

B.p. 98-99° (16 mm) n_D^{20} 1.4649, d_4^{20} 0.9465, MR_D 45.33; calc. 45.21.
Literature data [11]: b.p. 92° (10.5 mm), n_D^{20} 1.4672, d_4^{20} 0.9504.

The methiodide was obtained in 85% yield. It melted at 154° (from anhydrous alcohol), and gradually solidified; second m.p. 258°. Literature data [8]: m.p. 152-153°, solidifies at 160°.

Hydrazone of 4-dimethylamino-2-butanone. 16 g of aminoketone (I) was added, with stirring, to 10 ml of hydrazine hydrate. The hydrazone was salted out with solid alkali, and was then extracted 3 times with ether, dried with fused potassium hydroxide, and distilled under vacuum in a stream of nitrogen. The yield was 12.3 g (68.3%).

B.p. 94-95° (12 mm), n_D^{20} 1.4789, d_4^{20} 0.9170, MR_D 39.85; calc. 39.92.*
Found %: C 55.94, 55.80; H 11.97, 11.78. $C_7H_{15}N_3$. Calculated %: C 55.77; H 11.70.

The action of concentrated hydrochloric acid on the isolated hydrazone of aminoketone (I) gave white crystals of hydrazine hydrochloride. M.p. 198° (which agrees with the literature data). The action of benzaldehyde on this hydrazone gave, in quantitative yield, benzaldehyde azine with a m.p. of 93°, which also agrees with the literature data.

3-Methylpyrazoline (II). To 60 ml of hydrazine hydrate was added, with stirring and over a period of 0.5 hour, 128.5 g of the methiodide of aminoketone (I) in the form of a suspension in 140 ml of methyl alcohol (the temperature of the exothermic reaction rose to 40-45°). The mixture was stirred for 0.5 hour at room temperature and for 20 minutes while heating to boiling, cooled, and the precipitated salt was filtered and carefully washed with ether; this ether was used for the subsequent extraction. The methyl alcohol was distilled from the filtrate under vacuum and in a stream of nitrogen; the residue was made alkaline with solid alkali, and extracted with ether for 10 hours in a liquid extractor. The ethereal solution was dried with potassium carbonate, and distilled in a stream of nitrogen. The yield was 11.5 g (27.2%).

B.p. 60-62° (24 mm), n_D^{20} 1.4732, d_4^{20} 0.9653, MR_D 24.45; calc. 24.34.**

* The atomic refraction of the hydrazone nitrogen was taken as 2.47; 3.6 was used for the imine nitrogen.
** The refraction for the =N−N− group in all pyrazolines was taken as 5.781 [12].

Further extraction (10 hours) of the aqueous residue with ether separated an additional 1.3 g of the pyrazoline. The total yield was 12.8 g (30.4%). N-phenylcarbamide derivative of the pyrazoline: m.p. 110° (from alcohol). Literature data [13]: for the pyrazoline, b.p. 56° (15 mm); for the N-phenylcarbamide derivative, m.p. 109°.

3-tert-Butylpyrazoline (III). Prepared analogously to (I) from 45 ml of hydrazine hydrate and 81 g of the methiodide of aminoketone (VI) in 75 ml of methyl alcohol. The pyrazoline was isolated by 3-fold extraction with ether. The yield was 16.3 g (48.4%).

B.p. 64° (7.5 mm), n_D^{20} 1.4673, d_4^{20} 0.9148, MR_D 38.30; calc. 38.19.

The N-phenylcarbamide derivative was readily soluble in alcohol and ether. M.p. 61.5-62° (from petroleum ether).

Found %: C 68.71, 68.75; H 7.91, 7.94. $C_{14}H_{19}ON_3$. Calculated %: C 68.54; H 7.80.

The N-benzoyl derivative was obtained in 61% yield by acylation of the pyrazoline with benzoic anhydride in anhydrous benzene. M.p. 82° (from petroleum ether).

Found %: C 73.00, 73.05; H 8.03, 7.89. $C_{14}H_{18}ON_2$. Calculated %: C 73.01; H 7.86.

3-Ethyl-4-methylpyrazoline (IV). Prepared similarly to (III) from 50 ml of hydrazine hydrate and 105 g of the methiodide of aminoketone (VII) in 100 ml of methyl alcohol. The yield was 17.9 g (42.1%).

B.p. 66-67° (10 mm), n_D^{20} 1.4709, d_4^{20} 0.9310, MR_D 33.66; calc. 33.58.

N-α-Naphthylcarbamide derivative, m.p. 87° (from petroleum ether).

Found %: C 72.40, 72.52; H 6.95, 7.04. $C_{17}H_{19}ON_3$. Calculated %: C 72.57; H 6.80.

3,4-Tetramethylenepyrazoline (V). Prepared by the same method from 45 ml of hydrazine hydrate and 90 g of the methiodide of aminoketone (VIII) in 85 ml of methyl alcohol. The yield was 14.1 g (38.1%).

B.p. 104-105° (12 mm), n_D^{20} 1.5184, d_4^{20} 1.0376, MR_D 36.29; calc. 36.00.

The N-phenylcarbamide derivative melted at 106° (from aqueous alcohol).

Found %: C 69.12, 69.18; H 7.10, 7.14. $C_{14}H_{17}ON_3$. Calculated %: C 69.11; H 7.04.

The N-benzoyl derivative was prepared in 62.3% yield by acylation of the pyrazoline with benzoic anhydride. M.p. 74.5° (from petroleum ether).

Found %: C 73.65, 73.92; H 7.07, 7.27. $C_{14}H_{16}ON_2$. Calculated %: C 73.66; H 7.06.

SUMMARY

A new method for the synthesis of 3-alkyl- and 3,4-dialkylpyrazolines is described, the basis of which is the reaction of hydrazine hydrate with methiodides of β-dimethylaminoketones.

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INVESTIGATION OF THE VOLATILE SUBSTANCES OF GARLIC

A. M. Khaletsky and M. B. Reznik

The use of garlic as a medicinal remedy has long been known [1]; as regards the chemical nature of the substances contained in it, substances which act destructively on the various causes of illness, this question has been insufficiently studied. In connection with the recently discovered antibacterial properties of garlic with respect to staphylococci, enteric fever, Siberian ulcer, and tuberculosis bacilli, sarcina, cholera vibrio and others, and also with respect to the ability of the volatile substances of garlic to act on the causes of illness at a distance [2], it seemed of interest to study closely the volatile substances contained in it.

It should be noted that Wertheim [3], studying the essential oil of garlic, found allyl sulfide in it. Semmler [4] studied this oil in greater detail, and found propyl allyl and diallyl disulfide, diallyl trisulfide, and diallyl tetrasulfide. Cavallito and co-workers [5] isolated diallyl sulfoxide sulfide [allyl allylsulfinyl sulfide] from garlic, calling it allicin, and Stoll and Seebeck [6] reported the isolation by them of the oxide of allylcysteine. In the opinion of Rundquist [7], the essential oil of garlic is associated with sugars, and, in the presence of the enzyme alliase, it undergoes cleavage into the sugar and aglycone similarly to glycosides. A similar proposal by Toroptsev [2] finds basis in the fact that on heating, to 37°, for example, activation of the enzyme increases and the protistacidal activity of the tissue juice of garlic is strengthened.

However, it is impossible to form, from a review of the literature, final conclusions relative to the nature of the volatile substances occurring in garlic. On the other hand, any action by chemical agents or by temperature promotes a change in the change in the chemical nature of the volatile substances. Therefore, it appeared to be of interest to obtain the essential oil of garlic in its native state, something which appeared possible to accomplish by passing an inert gas (nitrogen) through it at ordinary or low temperatures, thereby excluding the effects of atmospheric oxygen and high temperatures.

It should be noted that the volatile substances are liberated from garlic in very small amounts, hence, in order to accumulate it, we developed special methods based both on tying up these substances with a solution of mercuric chloride and by cooling them to −70 to −80°. The substances obtained from garlic by distillation in a current of nitrogen and by steam distillation were not identical; they were different not only with respect to their behavior toward Grote's reagent, but even organoleptically. Thus, the volatile substances obtained by steam distillation have a disagreeable odor and a yellowish brown color, while those obtained by distillation in a stream of nitrogen had the odor of garlic and were colorless. From the quantitative content of mercury and sulfur in the organomercury compound and also from the amount of hydrogen chloride formed during the interaction of the volatile substances of garlic with mercuric chloride, the following structure can be ascribed to the organomercury compound:

$$CHHgCl{=}CHgCl{-}CH_2{-}\underset{\underset{O}{\|}}{S}{-}CH_2{-}CHgCl{=}CHHgCl.$$

EXPERIMENTAL

Organomercury complex of volatile substances in garlic. In an extractor composed of a glass vessel consisting of two ground glass halves fitted with outlet tubes was placed 1-1.5 kg of powdered garlic. At one end,

the extractor was connected through the outlet tube with a system of absorption vessels containing 20-25 ml of a 5% solution of mercuric chloride; at the other end, it was connected with a nitrogen cylinder. The volatile substances of the garlic were entrained by virtue of the increased pressure of the nitrogen flowing through the vessel, and were carried over into the absorption vessels. The formation of turbidity was first observed in the absorption vessels, followed by the appearance of a precipitate, the greatest amount being formed in the first vessel. When the nitrogen was fed at an average rate of 25-30 liters per hour, accumulation of volatile fractions of the garlic was observed over the course of a day and longer, which is in agreement with literature data on the gradual liberation of volatile material over the course of a long period of time. Since, however, formation of volatile products as a result of fermentation of the garlic was not excluded, collection of the volatile products was carried out for not more than 24 hours. After separation of the precipitate and washing it with hot and then cold alcohol to a negative reaction for chloride and mercury ions, it was dried in the extractor to constant weight. The precipitate was a white, light-weight powder without odor and insoluble in water, alcohol, ether chloroform, acetone, and ethyl acetate; it charred at 200° without melting. On heating, mercuric chloride sublimed, and on treatment with hydrochloric acid, the odor of garlic was detected. The substance did not dissolve in acids or in solutions of mercury iodide or cyanide; it assumed a yellow color under the influence of alkali, and darkened on heating.

The emergence of a garlic odor when acted on by 10% hydrochloric acid indicated decomposition, and therefore, the presence of a mercury-containing group, which was confirmed by its behavior toward potassium iodide – solution occurred, apparently owing to the formation of K_2HgI_4. In addition to mercury, sulfur and chlorine were detected in the organomercury compound by qualitative reactions; sulfur was shown by oxidation to sulfate and precipitation as barium sulfate; chlorine was detected by the formation of sodium chloride on treatment of the material with metallic sodium and by the formation of silver chloride under the influence of silver nitrate. During investigation of the filtrate, hydrochloric acid was observed as a product of the interaction of the volatile substances of garlic with $HgCl_2$, indicating the presence of a substitution reaction with the formation of hydrogen chloride.

Grote's reagent [8] (sodium nitroprusside and hydroxylamine) was used to determine the nature of the bonds of the sulfur with the other elements in the volatile substances of the garlic; however, a change in color was not observed, which indicated the absence of $-C-S-S-C-$ bonds and the possible presence of $-C-S-C$ or $-C-S-S-C-$.

On reaction with Walker's reagent [9], a weak rose color appeared only after a long time; on the contrary, the essential oil obtained by steam distillation of the garlic formed a red color with Grote's reagent, which indicated the presence of $-C-S-S-C-$ bonds.

0.1-0.2 g of the organomercury complex, which had been dried to constant weight in a vacuum desiccator was mixed with 15 ml of 25% hydrochloric acid and 10 ml of bromine water in a 100-ml round-bottomed flask fitted with a reflux condenser connected by a ground glass seal, and heated on a sand bath until solution was complete.

After the introduction of water through the condenser to wash off sublimed mercuric chloride, the solution was transferred to a 250 ml flask, the excess bromine was removed with a stream of nitrogen, and the residue was diluted with water to a concentration of the hydrochloric acid of 0.3-0.4 N. The solution was saturated with hydrogen sulfide, the precipitate (HgS) transferred to a weighed Gooch crucible, washed with water and alcohol, and dried at 110° to constant weight.

Found%: Hg 74.62; S 2.94; Cl 14.01. $C_6H_6OSHg_4Cl_4$. Calculated%: Hg 74.77; S 3.03; Cl 13.25.

By a determination of the amount of hydrogen chloride liberated by the interaction of mercuric chloride with the volatile substances of garlic, the following data were obtained: organomercury complex formed, 0.4832 g (97.5%), 0.3816 g (97.6%), 0.5026 g (100%), from which it follows that 1 mole of volatile substances from garlic reacts with 4 moles of mercuric chloride.

Isolation of the volatile substances of garlic at low temperatures was carried out by passing nitrogen through the powdered garlic and cooling the volatile substances to from −70 to −80° and separating the condensed water.

In this manner, about 1 ml of a turbid liquid with the sharp odor of garlic and soluble in ether was obtained from 1-1.5 kg of garlic. By cooling an ethereal solution with solid carbon dioxide to −30 to −40°, separating the ice crystals by filtration, and distillation of the ether under vacuum, about 0.3 g of a material with a neutral reaction and the odor of garlic was obtained. On the addition of 1 ml of mercuric chloride (in the presence of NaCl) to 2-3 drops of an alcoholic solution of this material, the formation of a white precipitate along with the emergence of an acid reaction was observed. Color did not appear on reaction with Walker's reagent, and only on heating did a reddish color appear, apparently under the influence of atmospheric oxygen and other processes. Thus was it shown that the native volatile substances of garlic are different from the volatile substances obtained by steam distillation.

Comparative microbiological investigations with paramecium of the volatile substances of garlic obtained both at ordinary and at low temperatures (in a stream of nitrogen showed that these materials are 20 times more active than the volatile substances obtained by steam distillation of garlic.

SUMMARY

1. The volatile substances contained in the native garlic were investigated, and it was shown that they contain diallyl sulfoxide by the formation of tetramercuritetrachlorodiallyl sulfoxide.

2. It was shown that the volatile substances obtained from garlic by steam distillation differ from the native volatile substances present in garlic.

3. Methods were developed for the recovery of volatile substances from garlic both with the aid of mercuric chloride and by distillation in a stream of nitrogen at low temperatures.

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FOR DISCUSSION

IN CONNECTION WITH A. BUNDEL'S OBSERVATIONS ON THE ARTICLES "THE PARTICIPATION OF OXYGEN IN THE FORMATION OF ZINC SULFIDE PHOSPHORS" AND "THE CHEMISTRY OF FORMATION OF LUMINESCENT CENTERS IN ZINC SULFIDE PHOSPHORS"

N. Ril and G. Ortman

The Journal of General Chemistry [26, p. 1512 (1956)] contained observations by A. Bundel on our articles published in 1955.* Unfortunately, these observations somewhat distort the content of the articles and are based on personal hypotheses and not on facts. Thus, A. Bundel asserts that we used "an insufficiently pure specimen of zinc oxide," and in this connection quotes the analysis results given by us.

It is clear from the text of the articles, however, that in the majority of cases we did not use these "insufficiently pure specimens." The analysis results for these specimens were given by us as examples of those sharp deviations from stoichiometric composition which are observed if special precautions are not taken to remove impurities (particularly oxygen). All the main experiments were carried out on sulfide which had been previously treated with dry hydrogen sulfide at 500° and checked by analysis for the absence of impurities.

A. Bundel writes that in the experiments on activation by copper at low temperatures we used zinc sulfide "ignited in air" at 1200°. There was not even any mention of ignition in air at 1200° in our articles. (A. Bundel probably meant the specimens prepared by the ordinary crucible method at 1250°.) Later, A. Bundel introduces into his criticism the arbitrary hypotheses of "deep oxidation" of our specimens and other hypothetical impurities. His criticisms would have been more useful had he become more accurately acquainted with the contents of our articles, in which a study was made of the sources of oxygen contamination of the specimens and in which we noted the insufficient care taken by a number of authors in carrying out their experiments and in relying, without check, on the purity of the gases which they used, the absence of moisture in the HCl vapor, etc. (Our criticism of the results of other authors was based, in the majority of cases, not on some sort of general considerations but on the repetition of their tests and on experimental checking of their results.)

From the description of our experiments on the preparation of activator-free zinc sulfide in the absence of oxygen, it should have been clear that the measures which we adopted to ensure the absence of oxygen (preliminary treatment of the sulfide with dry hydrogen sulfide at 500°, removal of occluded gases by exhaustion in vacuo, removal of moisture from the flux by remelting it, the use of spectroscopically pure nitrogen, etc.,) were far more thorough than any adopted by other authors. It is clearly pointed out in our article that we obtained that data on the influence of oxygen using the second method not because we doubted the reliability of the first method, but because we doubted whether the action of oxygen was direct or indirect (see page 1064.)

The lack of care with which A. Bundel has composed his remarks can be seen from the fact that he points especially to the high volatility of zinc at 900°, not noticing that in our article this fact is particularly emphasized (see page 1291.)

The only observation which in our view might be considered valid is the remark that the fact that the specimen turned gray - under the action of dry HCl vapor does not prove that zinc has been liberated. But even here A. Bundel confines himself to the general hypothesis that the production of the gray color may be taking place on account of some impurity, without giving even one example of an impurity which might, in fact, give the specimen a gray color, and in so doing loses sight of the fact that the production of the gray color is only observed in dry HCl vapor.

* See J. Gen. Chem. 25, 1057, 1289(1955).

Our main experiments on the precipitation of ZnSCu-luminophors by ignition in hydrogen without melting are not mentioned by A. Bundel at all.

It seems to us that the material contained in our articles may throw some light on the problem and does not give A. Bundel grounds for being influenced by personal hypotheses.

The results of our studies will be published in more detail in Monograph No. 72 as a supplement to the Journal "Angewandte Chemie."

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